

# The Molecular Identification of Organic Compounds in the Atmosphere: State of the Art and Challenges

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## 1. Introduction

The Earth's atmosphere offers a striking contrast with other planets or other environments in the universe by its rich organic composition, which results almost exclusively from the presence of life on the planet. About 2000 Tg/yr of organic compounds are estimated to be emitted into the atmosphere as gases, another 300 Tg/yr as particulate matter (aerosols), and a smaller, yet non-estimated, fraction is dissolved in cloud or fog droplets. While these quantities represent only a few percent of the total carbon budget, dominated by CO<sub>2</sub>, they represent a diversity of 10<sup>4</sup> to 10<sup>5</sup> distinct compounds,<sup>1</sup> which play essential roles in many atmospheric processes. The importance of organic gases (or Volatile Organic Compounds, VOCs) in air quality and tropospheric ozone formation was recognized as early as the 1950's,<sup>2</sup> while their role in the atmospheric radical cycles was evidenced in the 1970's.<sup>3</sup> Then, their role as precursors for secondary organic aerosols (SOAs) started to be unveiled in the 1980's and 1990's and, for the last two decades, their contribution to the Earth's radiative budget, through their optical and cloud-forming properties, has been discussed and is progressively taken into account in the projections of the Intergovernmental Panel for Climate Change (IPCC). This growing realization of the importance of these compounds in the atmosphere has been accompanied by an exponential increase of the research activities and scientific articles on this subject, making of organic compounds a main research area in atmospheric science today.

To a large extent, understanding the processes involving organic compounds in the atmosphere depends on how well these compounds are identified. But obtaining this information for atmospheric samples involves a number of challenges, such as their collection, separation, decoupling of meteorological and chemical processes, small masses, complex mixtures, and low concentrations of individual compounds. New instruments have thus been developed and

analytical techniques from other disciplines modified to overcome these problems. These efforts started slowly in the 1970's and 1980's but have undergone a tremendous evolution over the last decades. This review presents a state-of-the-art account of this rapidly expanding field of atmospheric organic compound identification. In particular, it presents an overview of the core concepts in analytical chemistry and provides guidelines and recommendations on the performances and limits of different techniques that are aimed at the wide range of scientists with diverse backgrounds studying these questions today (physicists, meteorologists, chemists, biologists, engineers, etc).

Chapter 2 of this review introduces the main definitions related to molecular identification, and discusses the different degrees of identification required by atmospheric problems or offered by techniques. Chapter 3 presents the strategies to ensure the quality of the analyses in atmospheric sciences. Chapter 4 summarizes the different techniques available today or under development to characterize atmospheric organic compounds and their various levels of identification. Chapter 5 presents current key questions involving organic compounds in atmospheric science and approaches to solve them. Finally, Chapter 6 summarizes the main trends, current challenges, and potential future directions of this field of research.

## **2. Definitions and application to the atmosphere**

### **2.1. Molecular identification: definitions**

Before discussing organic identification in atmospheric chemistry and how to achieve it, it is important to give some definitions. An organic compound is fully identified only if its molecular structure is entirely known, including its isomeric and spatial (stereo) configuration. While this information can be obvious for small molecules ( $C_1$ ,  $C_2$ ) it becomes increasingly challenging to obtain as their size and molecular weight (MW) increase. Furthermore, full structural identification

usually requires different types of analyses, such as some focusing on the molecular composition and others on the structure.

Scientific societies such as the International Union for Pure and Applied Chemistry (IUPAC), the American Chemical Society (ACS), the American Society for Mass Spectrometry (ASMS), and journals thus require the identity of isolated organic compounds to be supported by a minimum of two types of information, such as the molecular weight and the structure. An additional challenge in environmental sciences is to identify organic compounds present in complex mixtures. The most common method employed to solve this problem is chromatographic separation, which, combined with comparison of their chromatographic and mass spectrometric behaviors with those of reference compounds (or standards), can also lead to unambiguous identification.

As discussed in Chapter 4.2.3, the MW of a compound is the basis to determine its molecular formula, by comparison with the exact weights of various theoretical formulae. The number of matching theoretical formulae depends on the accuracy with which the measured MW is determined and increases exponentially with MW. Knowing the elements present in the molecule, for instance that they are limited to C, H, O, S and N, reduces the number of matching formulae. Scientific societies, in particular the ASMS have thus established that a molecular formula is elucidated if the accuracy on the measured MW corresponds to a single matching formula. Thus, in the absence of other complementary information, current high-resolution MS techniques can only identify a formula for compounds up to  $300 - 350 \text{ g mol}^{-1}$ .<sup>1</sup> Beyond this, and in some cases for lower MW,<sup>4</sup> the identification requires additional information such as isotopic composition or fragmentation (tandem MS). As explained above, chromatographic separation and comparison of their chromatographic and mass spectrometric behaviors with those of authentic standards also

solve these problems. In this case, the comparison between the compounds in the sample and authentic standards must be made with sufficient accuracy.

Beside the elemental composition given by the molecular formula, the full spatial structure of organic compounds, i.e., their different isomers or spatial configurations, can be obtained from NMR techniques (Chapter 4.1), or tandem MS (Chapter 4.2.3) (successive fragmentation of the precursor ion). Chromatographic methods and comparison with an authentic standard can also provide full structural information if suitable standards are available (i.e., in the form of specific isomers). The full structural identification of an unknown molecule is therefore a considerable analytical challenge, especially in complex environmental samples.

## **2.2. Describing the level of identification: factor “*I*”**

Not all atmospheric problems require the full identification of organic compounds. Intermediate levels of identification exist, focusing on specific classes of compounds or functional groups, and which can be sufficient to answer many atmospheric problems. In this review the level of identification required by a problem or offered by a technique will be described by a “Factor *I*” defined as:

*I* = number of possible molecules matching the information requested or measured by a specific analytical technique.

Thus by definition full identification is equivalent to  $I = 1$ . However if a compound has two or more isomers that are not separated then  $I = 2$  or higher. For instance, the 2-methyltetrols, which have been found in many aerosols and were proposed as secondary products of isoprene have isomers (diastereoisomers), 2-methylerythritol and 2-methylthreitol, each of them having two enantiomers (mirror-image isomers). Thus, the exact MW of these compounds identifies them with only  $I = 4$ . Using non-chiral gas chromatography (GC) columns can separate the two isomers, thus



identify them with  $I = 2$ .<sup>5</sup> Finally, separation on chiral columns can distinguish each enantiomer and identify them with  $I = 1$ .<sup>6</sup> Typically, for a compound with a MW determined by MS  $I =$  number of molecules matching MW  $\times$  number of possible isomers and spatial configurations. By contrast, optical spectroscopies generally result in the identification of organic compounds with large  $I$  factors. For example, the analysis of mixtures from secondary organic aerosol products by infrared (IR) spectroscopy only gives the relative distribution and temporal evolution of functional groups.<sup>7</sup> While this provides some overall information on the bulk composition, no structural information on specific compounds can be derived. Similarly, with MS using hard ionization techniques such as electron ionization with 70 eV electrons the very large number of fragments introduce large uncertainties in the determination of the MW of specific compounds and for the identification of their structure.

Factor  $I$  will be used throughout this review to describe the levels of identification offered by different techniques (Chapter 4) or required by specific atmospheric problems (Chapter 5).

### **2.3. How well do atmospheric organic compounds need to be known?**

Trying to identify all the organic compounds present in the atmosphere would not only be a staggering task but also largely redundant as many problems can be solved with only a partial knowledge of these compounds. Different type of problems, corresponding to different levels of information, can be distinguished.

**Inventorying compounds according to their properties ( $I \geq 100$ ).** The first type of problem is when organic compounds need to be inventoried for the purpose of establishing a budget. Generally, such budgets are required to gain insights into specific properties of the compounds, such as their optical properties for the global energy budget or their volatility for SOA precursors. In such cases the organic compounds do not need to be individually identified but their effects

only quantified based on this common property. These questions can thus be solved by performing functional group analyses (Chapter 4.1), which would provide identification with  $I \geq 100$  (probably even  $\geq 1000$ ).

**Capturing chemistry in a turbulent atmosphere: real-time monitoring ( $10 \geq I \geq 100$ ).** A common problem in atmospheric chemistry is the investigation of chemical processes or sources in a rapidly changing environment (boundary layer height changes or influence of different air masses). This type of problem does not necessarily require the full identification of the organic compounds either but demands that the analytical techniques characterize organic compounds on time scales of seconds to minutes. For this purpose, “on-line” instruments have been developed to monitor gaseous or particulate organic compounds in real-time (Chapter 4.2.1). In spite of the fast measurement frequencies, the identification of gases with such techniques can be adequate when combined with high-resolution MS techniques ( $I \leq 10$  with proton transfer (PTR) – time-of-flight (TOF) MS, Chapter 4.1). Some real-time aerosol measurements however use hard ionization techniques (Chapter 4.1), resulting in extensive fragmentation and precluding in-depth identification of the organic compounds ( $I \geq 100$ ).

**Monitoring known processes or sources: relative identification ( $I \leq 10$ ).** A category of problems requiring a higher level of knowledge of the organic compounds is when known processes (for instance, chemical reactions) or sources need to be monitored or quantified in a given region of the atmosphere. An example is the quantification of the SOA mass resulting from one specific precursor, such as isoprene or  $\alpha$ -pinene, at a given site. The approach usually employed consists in monitoring a few compounds that are unique to these processes or sources, called “markers” (Chapter 3). The compounds present in the atmospheric samples do not need to be fully identified but only have to match the properties of the reference compound characterized

in laboratory. Such comparisons are often carried out by chromatographic methods (Chapter 4.2.2) whereby the chromatographic and mass spectrometric behaviors of the targeted and reference compounds are compared. For small compounds an identification based solely on direct MS can be considered, provided that sufficient resolution can be achieved. However, such an approach does not warrant the full identification of a compound, as the technique used does not necessarily distinguish between different stereo- and positional isomers.

**Identifying unknown processes or sources: full identification ( $I \leq 2-3$ ).** Atmospheric problems for which organic compounds need to be fully identified include those in which an unknown process or source is investigated. For instance, identifying specific organic products in aerosols gives some clues on the reactions taking place in these aerosols. Similarly, the identification of the organic compounds co-nucleating with sulfuric acid in the atmosphere is essential to understand the mechanisms of new particle formation (Chapter 5.5). In these cases it is necessary to aim at the maximum level of identification of the organic compound, which is only possible by combining different approaches or techniques (Chapter 4.2). By definition this level of identification corresponds to very small  $I$  values, ideally 1. The upper limit of 2 to 3 indicated above only accounts for potential stereoisomers of the same molecule.

### **3. Coping with atmospheric complexity**

#### **3.1. Sampling gaseous and particulate material**

Sampling is the first step of the characterization of compounds, both in the gas and the particle phase, and the choice of sample collection and preparation methods and appropriate analytical techniques can be crucial for their identification. This section aims to provide information on the sampling techniques for gaseous compounds and particulate material, and on the challenges and difficulties associated with the molecular identification of selected analytes.

### **a) Sampling of gaseous compounds**

VOC are commonly monitored in indoor and outdoor air. Methods for air sampling should leave the composition of the samples unaltered until analysis, be suitable for the type and concentrations of the compounds of interest and allow to carry out the analysis with sufficient sensitivity, accuracy, selectivity, precision, and cost efficiency. Various such techniques are available, including “whole air sampling”, where air samples are collected in containers, sampling on solid adsorbents, and continuous air sampling and on-line techniques. An overview of these sampling methods has been presented in previous review articles,<sup>8</sup> and only a short summary will be made here.

With “whole air sampling”, stainless steel canisters and Tedlar bags are the main containers used and they give rise to different potential artifacts. Canisters can keep air samples unaffected for up to 30 days until analysis, whereas Tedlar bags generally require the analysis to be performed within 24–48 h. While samples collected in Tedlar bags can be subject to permeation through the walls and degradation due to sunlight, those collected in stainless steel canisters are mostly affected by sorption and reaction on walls, which hamper the sampling of reactive compounds or those prone to isomerization. However, canisters<sup>9</sup> are widely used, especially for very volatile and non-polar compounds.<sup>10</sup> Their wide use in air monitoring has resulted in the development of a number of protocols for the analysis of a broad range of VOCs (e.g., the US Environmental Protection Agency methods TO-14, TO-14A, TO-15 and ASTM D-5466).

Sampling by adsorptive enrichment can be used both for sampling itself and for pre-concentrating the VOCs prior to GC/MS analysis, as summarized in review articles.<sup>11</sup> They are followed either by thermal desorption or solvent extraction, depending on the type of compounds studied. No single sorbent or extraction technique is suitable for the entire range of ambient VOC

volatilities and polarities. Use of a combination of different sorbents, in increasing order of adsorbent strength, partly addresses this challenge. In addition, co-trapped atmospheric oxidants (e.g., ozone) can lead to interferences by reaction with the sorbent material or with the trapped VOCs. Samples with high water content are also a problem, not only for the adsorbing materials but also for the subsequent analysis, e.g., by accumulation in the cryogenic traps which are used for pre-concentration prior to GC analysis. The addition of derivatization reagents on solid sorbents, cartridges or denuders, or into a trapping solvent in impingers, can increase the selectivity of the sampling towards targeted compounds. Such methods are used, for instance, for the determination of semi-volatiles, i.e., carbonyl compounds by using 2,4-dinitrophenylhydrazine as the derivatization agent.

Continuous and on-line sampling methods for VOCs avoid most of the sampling artifacts described above. New developments for these methods include miniaturization and techniques enabling higher time resolution or sensitivity, which have a potential for laboratory automation or on-site analysis. Examples include in-needle trap devices that allow for potential solvent-free sampling/sample preparation and introduction devices,<sup>12</sup> or are used in direct coupling to mass spectrometry, i.e., fiber introduction mass spectrometry.<sup>13</sup> Also membrane-based methods, such as membrane inlet mass spectrometry<sup>12,14</sup> or membrane extraction with a sorbent interface<sup>13,15</sup> have been described.

In conclusion, a wide range of parameters has to be taken into account when selecting an appropriate sampling method, including the chemical properties of the target analytes, the complexity of the sample matrix, and the compatibility of the sampling method with various extraction and analytical techniques

#### **b) Sampling of particulate material**

Sampling of particulate organic material (organic aerosols) is generally accomplished by collection on filter samplers or, to a lesser extent, with cascade impactors (e.g., MOUDI;<sup>14</sup> DLPI, [www.dekati.com](http://www.dekati.com)). The topic has been the subject of review articles<sup>16</sup> and addressed in textbooks,<sup>17</sup> thus only a brief overview will be presented here, with emphasis on sampling artifacts and gas-/particle-phase distribution.

The choice of the filter material on which the samples are collected is critical. When the samples have to be analyzed by thermal-optical analysis<sup>18</sup> for total organic, elemental and total carbon (OC, EC and TC), quartz fiber filters are mandatory because they are the only type able to sustain high-temperature treatments. Otherwise, other materials can also be used, e.g., polytetrafluoroethylene (Teflon®), or aluminum foil in cascade impactors. However, they all give rise to artifacts. In particular, all filter types can result in negative artifacts as the particulate-phase organics collected on the filter may volatilize during sampling. It was suggested that about 40% of aerosol carbon is volatilized during sampling,<sup>19</sup> but losses up to 80% have also been reported.<sup>15a</sup> Quartz fiber filters are also prone to positive artifacts due to their large adsorption capacity for volatile and semi-volatile organic compounds.<sup>16</sup> Several approaches have been proposed to avoid or to assess these artifacts. They vary from the simple use of double quartz filters (so called Q1Q2 or QBQ set-ups), to tandem filter set-ups<sup>16a</sup> or the use of denuders to remove organic and inorganic gases from the air sampled,<sup>20</sup> to more sophisticated systems such as the Brigham Young University organic sampling system and its variants,<sup>21</sup> where a denuder is used before the quartz fiber filter and an adsorbent bed (for collecting volatilized organics) is used after it.

Several studies have investigated the artifacts linked with the use of quartz fiber filters in the analysis of total OC<sup>22</sup> and for water-soluble OC (WSOC).<sup>22b</sup> But such studies have rarely been performed on individual organic species, with the exception of dicarboxylic acids (DCAs)<sup>23</sup> and

polycyclic aromatic hydrocarbons (PAHs) and related compounds such as polychlorinated biphenyls.<sup>24</sup> In addition, the gas-phase/particle-phase distribution of the species of interest has to be considered especially for long sampling durations. In a very recent study,<sup>23</sup> this distribution was found to be close to or higher than unity in summer for 2-methyltetrols and levoglucosan.

An alternative to collecting the particulate and gas phases separately is collecting the two phases together, as in a study reporting the measurement of a total of 180 compounds, including mostly *n*-alkanes, PAHs, and polar organic compounds, in field samples by GC/MS.<sup>25</sup> This approach has however the disadvantage that the information on the concentrations in each of the two phases is lost.

In summary, sampling artifacts and semi-volatile behavior exist for a number of particulate-phase organic species. Their extent depends on many parameters such as temperature, relative humidity, sampling site, sampler type, collection substrate, sampling duration and sampling face velocity, and vapor pressure of the species. Some species are also prone to specific artifacts such as organic acids, for which the sampling efficiency depends on the degree of neutralization. Artifacts may be avoided by using denuders upstream of the sampler or an absorbent pad (e.g., polyurethane foam) to collect the species that are desorbing during sampling. More studies of sampling artifacts are necessary, especially for the compounds used in source apportionment.

### **3.2. Standards and references**

In atmospheric chemistry, the identification of specific processes or sources requires full molecular identification and is often achieved by comparing specific tracers, or better marker compounds (see definition and discussion below in this section), to well-characterized reference compounds. Alternatively, when no authentic standards are available proxy compounds can be used but only for quantification. For example, since authentic organosulfate standards are not

commercially available, camphorsulfonic acid<sup>26</sup> sulfate is often used as surrogate standard for the quantification of  $\alpha$ -pinene-related nitrooxy organosulfates. In this section we provide information on commercially available reference standards and standards that have been synthesized and characterized by different research groups and used as marker compounds for specific scientific questions.

#### **a) Availability of authentic standards**

A number of molecules representing anthropogenic organic compounds such as linear and branched alkanes and alkenes,<sup>27</sup> alkynes,<sup>28</sup> aromatics, polycyclic aromatic hydrocarbons, and their oxygenated and nitro-substituted products<sup>29</sup> (e.g., nitro and hydroxy xylenes, nitro methylnaphthalene)<sup>29</sup> are available commercially. Some oxidation products for more complex molecules representing important atmospheric biogenic VOCs such as isoprene, monoterpenes (i.e.,  $\alpha$ -pinene,  $\beta$ -pinene, limonene, myrcene, terpinylene), and sesquiterpenes (i.e.,  $\beta$ -caryophyllene,  $\alpha$ -humulene,  $\alpha$ -cedrene,  $\beta$ -farnesene, etc.) are also available commercially. This is however not the case for many other of their oxidation products. Table 1 gives an overview of reference standards for such compounds, which are not commercially available, but have been synthesized and characterized in non-commercial laboratories using a variety of analytical techniques.

#### **b) Synthetic approaches towards authentic standards for analysis**

The identification of an unknown compound in ambient or laboratory-generated samples requires the use of authentic standards. However, many authentic standards are not commercially available, especially compounds that are specific to atmospheric chemistry or have been recently identified.

**Table 1.** Overview of synthesized reference standards for some atmospheric VOC reaction products. Acronyms: see list of abbreviations.



Precursor (class)	Marker compound	Characterization Method	Synthesis ref.	Lab/Field evidence ref.
<b>Hemiterpenes</b>				
isoprene	2-methylthreitol	GC/MS	30	30-31
	2-methylerythritol	GC/MS	30	30
	(2S,3R)-, (2R,3S)-, (2S,3S)-, (2R,3R)-2-methyl-tetrols	NMR, GC/MS	32	6,32b
	2-methylglyceric acid	GC/MS	30	30
	2-methylglyceric acid oligoesters, sulfates, nitrates	NMR	33	31,34
	methyl vinyl ketone, methacrolein sulfonates	HPLC/MS, 3Q-ESI-MS (on-line, off-line)	33	33
	cis- and trans-3-methyl-3,4-dihydroxytetrahydrofuran	NMR, GC/MS	35	35b
<b>Monoterpenes</b>				
$\alpha$ -, $\beta$ -pinene	3-hydroxyglutaric acid,	GC/MS	34,36	34,36
	3-methyl-1,2,3-butanetricarboxylic acid	GC/MS, HPLC/ESI-MS		
	<i>cis</i> -pinic acid	NMR	37	37
	hydroxy-pinonic acid	NMR	38	39
	hydroxy-pinonaldehyde	NMR	38	39
	terpenylic/terebic acid	HPLC/ESI-MS	39	30,40
	diaterpenylic acid acetate	NMR, HPLC/ESI-MS	41	41
	diaterpenylic acid	HPLC/ESI-MS	41	40-41
<b>Sesquiterpenes</b>				
$\beta$ -caryophyllene	$\beta$ -caryophyllene aldehyde,	NMR, GC/MS, ESI-MS	42	42
	$\beta$ -nocaryophyllene aldehyde			
	$\beta$ -caryophyllonic acid,	NMR, GC/MS, APCI-MS,	43	43
	$\beta$ -nocaryophyllonic acid,	HPLC/ESI-MS		
	$\beta$ -caryophyllinic acid,			
	3,3-dimethyl-2-(3-oxobutyl)-cyclobutanecarboxylic acid, 2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid			

This seriously hampers unambiguous structural elucidation. There are a number of manufacturers and/or fine chemicals suppliers that offer custom synthesis of authentic standards. Year by year this list expands, including small or medium-sized enterprises that have expertise with the synthesis of a narrow class of organics, e.g., Extrasynthèse offers a wide range of terpenes. Information about fine chemicals suppliers can be retrieved using on-line comprehensive databases, such as SciFinder® (a product of the ACS) and Beilstein® (a product of Elsevier B.V), or alternatively, using free-of-charge Internet resources, such as Chem Blink (<http://www.chemblink.com>) and Chemical Book ([www.chemicalbook.com](http://www.chemicalbook.com)). Because of the lack

of commercially available standards, research groups focusing on the molecular characterization of unknown organic compounds in the atmosphere have resorted to organic synthesis. Some studies have already demonstrated the value of organic synthesis to obtain reference compounds for hemi-,<sup>36</sup> mono-,<sup>34</sup> and sesquiterpene<sup>43</sup> oxidation products or potentially relevant light-absorbing species formed through simple reactions in aerosol mimicry.<sup>44</sup>

A useful approach to address the synthesis of an unknown compound in atmospheric research is based on retrosynthetic analysis of the target structure, a concept of molecular decomposition according to simple rules.<sup>45</sup> This approach involves the fragmentation of a target structure through a number of idealized molecular fragments denoted as synthons and continues until simple or commercially available structures are generated. Figure 1 shows an example of the retrosynthetic approach applied to the synthesis of 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), a marker for aged  $\alpha$ -pinene SOA.<sup>34,36</sup> It was not until 2007 that the structure of this unknown  $\alpha$ -pinene SOA marker with a MW of 204 was proposed and firmly confirmed using the latter approach (disconnection B in Figure 1).<sup>36</sup> In the synthesis of MBTCA,  $\alpha$ -bromoisobutyrate served as the synthetic equivalent for the electrophilic synthon, while alkyl succinate was selected as the synthetic equivalent for the nucleophilic synthon. Following the same strategy, MBTCA has recently been synthesized with high yield (78%) using methyl 2-methylpropanoate and dimethyl maleate as synthons.<sup>46</sup> The retrosynthetic synthesis approach could be applied to support the structural elucidation of other unknown compounds obtained from laboratory experiments or field studies.

In conclusion, targeted organic synthesis is a useful approach to support the unambiguous structural identification of unknown compounds in ambient aerosols and could be carried out either by commercial vendors or research laboratories using a variety of strategies. However, targeted

synthesis of the proposed compounds remains an expensive and/or a time-consuming task. Methods based on separation science can be employed instead. For instance, semi-preparative LC has been recently used as alternative approach to organic synthesis to obtain SOA markers from laboratory solutions for identification and quantification purposes.<sup>47</sup>

### **c) Assessing the atmospheric lifetime of marker compounds**

By definition an atmospheric tracer is “an entity which preserves its identity as it moves with the air from a known source, where the tracer is created or otherwise introduced into the atmosphere, to a known sink where it is destroyed or removed from the atmosphere”.<sup>48</sup> In this review preference has been given to the term “marker” instead of “tracer” as organic compounds in the atmosphere generally do not fulfill the requirement of preservation (e.g., due to reactions).

The identification of appropriate marker compounds for specific atmospheric processes is a difficult task due to the wide range of complexity and concentrations encountered in smog chamber and atmospheric samples. Important quality criteria for suitable marker compounds are reactivity, stability, and volatility (the latter only for markers of condensed-phase organic compounds).

For the markers of condensed-phase organic compounds volatility is one of the major parameters determining the atmospheric lifetime. Aqueous-phase reactions in clouds or condensed-phase reactions in aerosol particles can also be important for compound degradation, especially in the case of reactive species such as aldehydes. However, data on condensed-phase degradation or transformation processes is still very limited and subject of ongoing research and discussion. The atmospheric lifetimes for the markers of SOA from most precursors, including isoprene, monoterpenes, and aromatics are rather short (<1 day) (Figure 2) and are determined from their volatility, the latter being estimated from the number of carbon atoms and functional groups. A few exceptions to these short lifetimes include acidic sesquiterpene markers (estimated lifetime 2

– 10 days), the marker for aged  $\alpha$ -pinene SOA MBTCA (estimated lifetime  $\sim 10$  days), and oligomeric esters of acidic isoprene oxidation products (2-methylglyceric acid diester, estimated lifetime  $>10$  days).

### **3.3. Quality control and intercomparison**

Intercomparisons between different techniques or between operators have for objective to evaluate the analytical repeatability and reproducibility of the measurements and to highlight any bias or factor influencing the results. They are thus important for the quality control of the sampling and analysis method. For instance an interlaboratory comparison (ILC) allows laboratories to assess and demonstrate their performance in a particular test, calibration, or measuring sector. While several ILCs have been organized for the measurement of VOCs, very few have been organized for the measurement of aerosol organic compounds. However, an interlaboratory comparison has recently been organized for the measurement of levoglucosan, mannosan and galactosan within the European ACTRIS project.<sup>49</sup> The results evidenced small standard deviations between the measurements of levoglucosan, mannosan, and galactosan made by the thirteen participants. This ILC also revealed the lower detection limits of most GC/MS methods compared to those based on high-performance anion-exchange chromatography (HPAEC) with mass spectrometric or photodiode-array detection. In spite of the great benefits of ILCs for the quality of the measurements it is not realistic to propose such intercomparison activities to be organized for a large number of compounds. However, this would be desirable for major markers in ambient aerosol such as fungal spore markers (arabitol and mannitol) and biogenic SOA markers (2-methyltetrols, 2-methylglyceric acid for isoprene SOA; MBTCA, pinonic, pinic, terpenylic, and terebic acid for  $\alpha$ -pinene SOA).

## **4. The analytical tools**

In this chapter analytical techniques used and developed for the analysis of atmospheric trace gases and particles are described. First, in Section 4.1 one-dimensional techniques are presented, which consist in using only one physical-chemical property as parameter for the separation and identification of compounds, such as their optical or nuclear magnetic properties or molecular weight. In Section 4.2 multidimensional techniques are described which combine more than one one-dimensional technique and property for the identification, such as retention time in a chromatographic system and molecular weight measurement. In general multidimensional techniques offer a higher degree of identification (i.e., a lower *I* factor) than one-dimensional ones but are more challenging instrumentally. They also rely mostly on laboratory instruments whereas many of the one-dimensional techniques have been developed into on-line and field-deployable instruments. The main classes of techniques discussed in this review are compared in terms of their *I* factor in Figure 3.

#### **4.1. One-dimensional techniques**

##### **4.1.1. Optical and magnetic spectroscopies**

Optical and magnetic spectroscopies were classical identification techniques for atmospheric compounds before multi-dimensional techniques were developed. As they are based on the interactions of molecular functional groups with light or magnetic fields, optical and magnetic spectroscopies provide generally functional information, i.e., specific to chemical groups or bonds, rather than full structural information. However absorption spectroscopies (UV-Vis and FTIR) are suitable for the speciation of very small atmospheric organic compounds (C<sub>1</sub>, C<sub>2</sub>) and a greater variety of compounds has been successfully identified by emission FTIR spectroscopy.<sup>50</sup> Optical spectroscopies are also the only analytical techniques applicable to remote sensing. Their latest development over the last decade was in the form of cavity ring down spectroscopy and related

techniques, the sensitivity of which is considerably enhanced, and which allows for the detection and quantitation of atmospheric compounds in the low parts per trillion (ppt) or sub-ppt ranges. The techniques listed in Table 2 will only be briefly described in this paper, and the reader can refer to recent reviews and books<sup>51</sup> for a more comprehensive summary. The optical spectroscopies [FTIR, ultra-violet (UV)-Visible (Vis), etc.)] are described below, followed by nuclear magnetic resonance. Only one-step NMR methods are discussed in this chapter while the combination of NMR detection with chromatographic separation will be presented in Chapter 4.2.

**Table 2.** Non-mass spectrometric detection methods for atmospheric gas-phase organic compounds. Acronyms: see list of abbreviations.

Chemical species	Detection method	References
hydrocarbons	FTIR, GC-FID, CRDS, LP-DOAS (aromatics), chemiluminescence (alkenes)	50,52
HCHO	FTIR, DOAS, derivatization-fluorescence, LC/derivatization-UV	50,53
other OVOCs	DOAS, GC-FID and HPLC/UV techniques	54
PAN	FTIR, GC-ECD	55
halocarbons	FTIR, GC-ECD	56

#### a) FTIR and UV-Visible absorption spectroscopy

All organic molecules absorb light both in the IR (wavelength = 0.7 – 25  $\mu\text{m}$ ) and the UV- Vis (0.1 – 0.7  $\mu\text{m}$ ) region, which can be used for the characterization of their molecular structure. However, as the information obtained is mostly functional (i.e., specific to molecular groups or bonds) rather than structural, except for a few small molecules, absorption spectroscopies are more widely used for the quantification of known trace gases than for the identification of unknown compounds in the atmosphere.

In **IR spectroscopy** the spectral lines originate from the vibrational-rotational transitions of chemical bonds or functional groups in the molecules. The first important characteristic of these spectral lines, or bands, is their position in wavelength (or frequencies), which depends on the energy of the corresponding transition. Most of the absorption bands of interest for organics are between 500 and 4000  $\text{cm}^{-1}$  (near and mid-infrared region), while the high frequency portion ( $\geq 1300 \text{ cm}^{-1}$ ) displays the characteristic stretching bands of important functional groups such as OH, NH and C=O, and the ring bending absorption bands of aromatics appear below 900  $\text{cm}^{-1}$ . Absorption patterns in the intermediate region (1300 – 900  $\text{cm}^{-1}$ ) are more complex and specific to some molecules, and can therefore be used for identification (fingerprint region). In addition to frequencies, the width and shapes of the absorption lines are also important for both qualitative and quantitative measurements. In the condensed phase inter-molecular interactions make the IR absorption bands of organic compounds much broader than in the gas (spectral resolutions of the order of tenths  $\text{cm}^{-1}$ ) thus limiting their molecular identification. The characteristic *I* factor for solid-state FTIR spectroscopy is therefore very high ( $>10^2$ ) and this technique has been used mainly for laboratory studies,<sup>57</sup> functional group characterization and spectral fingerprints (similarly to NMR as discussed below).<sup>7b,58</sup> Organic gases, however, exhibit finer spectral features with typical line widths of 0.1  $\text{cm}^{-1}$  in the troposphere and of 0.01  $\text{cm}^{-1}$  in the stratosphere, providing a suitable tool for molecular identification and quantification.<sup>47b</sup> The measurements are either performed with a tunable solid-state laser or a broadband IR source and a FTIR spectrometer. The former allows for sensitive measurements in a narrow wavelength range, while the latter is used for molecular speciation but at the expense of sensitivity (roughly three orders of magnitude lower than lasers). Tunable solid state lasers are therefore used to identify and quantify simple organic molecules, such as CH<sub>4</sub>, CH<sub>2</sub>O, HCN, OCS and inorganic trace gases<sup>59</sup> while FTIR

spectrometry has been successfully applied to the speciation of a range of VOCs including CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>COOH, CH<sub>2</sub>O, CH<sub>3</sub>OH, HCN, HCOOH, C<sub>2</sub>H<sub>2</sub>, furan, and glycolaldehyde.<sup>50</sup> However, the poor detection limits (e.g., ca. 10 – 20 ppb for HCHO) make the FTIR method more suitable for laboratory applications or field measurements close to strong emissions, such as wildfires or prescribed fires.<sup>60</sup> An important advantage of FTIR spectroscopy over alternative methods for VOC analysis such as PTR-MS is the simultaneous detection of organic and inorganic trace gases (including H<sub>2</sub>O, CO<sub>2</sub>, CO, NH<sub>3</sub>, and HONO).

In **UV-Vis spectroscopy**, the absorption bands result from electronic transitions in the molecules and are fairly broad. Various types of electronic transitions can occur but those resulting in the highest molar absorptivity ( $\epsilon \geq 1000$ ) above 200 nm (i.e., the cut-off of most common solvents) are  $\pi \rightarrow \pi^*$  transitions and, in case of polyconjugations,  $n \rightarrow \pi^*$  transitions. The structural information obtained from UV-visible spectra in the condensed phase is very limited as the corresponding bands are not specific. This technique has thus been mainly used in combination with other techniques (e.g., LC-UV-Vis). But in the gas phase the combination of vibrational and electronic transitions greatly enhances the specificity of the bands. If the resulting spectrum contains sufficient fine structures with characteristic narrow bands ( $\leq 10$  nm), the technique can be very selective. Most applications of UV-vis spectroscopy to organic identification are limited to a few very simple molecules (HCHO, CS<sub>2</sub>), although larger molecules with strong chromophores (benzene, toluene, naphthalene, phenol, *p*-cresol) can be also observed. Thus, overall UV-Vis spectroscopy has a low capacity to identify unknown compounds, corresponding to *I* factors in the range of  $>10^2$ , and is mostly used to monitor known compounds. In addition, its lower sensitivity compared to modern PTR-MS instruments limits its atmospheric applications.<sup>52c</sup>



## **b) Differential optical absorption spectroscopy (DOAS) and cavity ring-down spectroscopy (CRDS)**

DOAS and CRDS are the latest developments of IR and UV-Vis spectroscopies, and have been designed to improve one of their weakest points: their low detection sensitivities. This is mostly done by extending the optical pathlengths. In its simplest configuration, long-path DOAS consists in a continuous light source, i.e., a Xe-arc lamp, placed at the focal point of a parabolic mirror generating a well collimated light beam and, at some hundreds of meters away, a telescope coupled to a detector. Absorption spectra of air molecules in the UV-Vis region are typically dominated by a broad-band signal caused by the Rayleigh scattering. Such signal must be subtracted to provide the characteristic narrow-band ( $\leq 10$  nm) absorption of the gases of interest (their “differential” spectrum).<sup>61</sup> These fine bands allow, in principle, DOAS to identify and quantify a wide range of gases. However, while this technique is routinely used to quantify inorganic trace gases ( $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ) and some VOCs, the identification of organic compounds is limited to a few small molecules, such as formaldehyde, glyoxal, methylglyoxal, and aromatic hydrocarbons.<sup>62</sup> The “open path” configurations normally employed for long-path (LP)-DOAS, were used to extend the pathlength also in IR spectroscopy.<sup>56b</sup> Beside the systems employing artificial light sources, passive measurements can be carried out with DOAS and IR spectroscopy by employing extraterrestrial light sources (the sun, the moon),<sup>57</sup> and typically over very long paths (several thousands of kilometers). Passive measurements are the principle of remote sensing. Thanks to the identification and characterization of VOCs in laboratory and in the field, DOAS is the only identification technique applicable to remote sensing and is widely used for the retrieval of the total column and vertical concentration profiles of many trace gases. Satellite DOAS sensors such as GOME and SCIAMACHY, measuring individual atmospheric trace constituents in the UV-Vis and near-IR

region and using recent characterizations of formaldehyde and glyoxal by these techniques,<sup>63</sup> have thus provided global concentration maps for these compounds.<sup>58</sup>

A further way to expand the optical pathlength and increase the sensitivity of atmospheric measurements is to flow the air samples through a closed cell where a laser beam is reflected between two highly-reflective mirrors. These multipass cells allow achieving pathlengths of 200 m with a cell, which is only 1-m long. Pathlengths of a few kilometers can be reached in cavity absorption spectroscopy and pulsed CRDS, employing a laser and a high-finesse optical cavity. In CRDS, the measurement is carried out after the light source is switched off, and the extinction produced by the substance of interest is determined from the decay of the intensity of the laser leaving the cell (the “ring-down”).<sup>64</sup> CRDS is mostly used in the atmosphere to monitor small inorganic molecules and their isotopic composition, but is, in principle, applicable to the analysis of (a few) C<sub>1</sub>-C<sub>2</sub> VOCs, as demonstrated in laboratory and some field conditions.<sup>59</sup> A further development of CRDS is cavity-enhanced DOAS, with which 10 - 40 km pathlengths are now routinely achieved. This has important benefits for the sensitivity of the technique, as it enables on-line measurements close to atmospheric conditions in laboratory settings.<sup>65</sup>

### **c) NMR spectroscopy**

Nuclear magnetic resonance spectroscopy is a *quasi*-universal technique for the analysis of organic compounds, and the main technique of reference to support the structural elucidation of organic compounds. It is however less used in environmental chemistry where sample loading can be too small to apply <sup>13</sup>C and heteronuclear NMR techniques. The general principles of NMR spectroscopy have been described in many text books.<sup>66</sup> The principle is that nuclei with a nuclear spin different from zero, such as <sup>1</sup>H, <sup>13</sup>C and <sup>15</sup>N, change orientation when subjected to an external magnetic field. But in addition to the “magnetic resonance” at the fundamental nuclei frequency

small deviations, of the order of a few part per millions (ppm), are induced by the chemical environment of the nucleus, thus providing local information on the structure of the molecule. Typical NMR spectra record these chemical shifts and allow to correlate one nucleus to another and to reconstruct the entire chemical structure. When only a limited number of compounds are present in a sample, stereoisomers can be differentiated, and *I* factors approaching 1 can be reached. Molecular identification in complex mixtures containing hundreds of resonances can also be performed with NMR but require procedures to reduce peak overlap. This can be achieved by increasing the magnetic field, hence reducing peak width and narrowing multiplets. Alternatively, series of samples from the same experiment can be analyzed by chemometric techniques (e.g., factor analysis) to attempt spectral deconvolution.<sup>67</sup> Finally, if sufficient amount of sample is provided (typically 1 mg of carbon), two-dimensional (2D) NMR techniques can also be applied, such as correlation spectroscopy or heteronuclear single quantum coherence or even heteronuclear multiple bond correlation,<sup>68</sup> which establish the connectivity between chemically-distinct H or C atoms in a molecule, and allow to reconstruct the chemical structure. Thus, 2D NMR has the potential to achieve low *I* factors even in complex compound mixtures.

However, while NMR spectroscopy is optimal for liquid samples, it is unsuitable to the analysis of gases and allows the analysis of amorphous solids only with a much lower resolution, i.e., with chemical shifts of around 100 KHz for <sup>1</sup>H-NMR.<sup>69</sup> Another advantage of NMR spectroscopy over other techniques is that quantitative spectra can be obtained relatively easily, especially with <sup>1</sup>H spectroscopy, as the line intensity is, in first approximation, directly proportional to the molar concentration of the nucleus of interest.

Unfortunately, the most interesting nucleus in organic chemistry, <sup>12</sup>C, has a nuclear spin of zero and is therefore NMR-silent. By contrast the isotope <sup>13</sup>C is magnetically active but because its

natural abundance is only 1.1% the sensitivity of  $^{13}\text{C}$  NMR spectroscopy is almost four orders of magnitude lower than that of  $^1\text{H}$  NMR. Thus the vast majority of NMR studies of atmospheric organic compounds is made with proton NMR techniques, and deal with aerosol extracts, cloud, fog or rainwater, or aqueous solutions of polar VOCs. It is worth noting that strong magnetic fields ( $\geq 600$  MHz) allow to resolve hundreds of resonances in atmospheric samples<sup>70</sup> with opportunities to discover new aerosol constituents.

A common assumption in atmospheric science is that the sensitivity of NMR spectroscopy is too low for a widespread application. While this is certainly true for  $^{13}\text{C}$  and heteronuclear NMR methods, and for the  $^1\text{H}$  NMR analysis of small aerosol volumes (e.g., in reaction chambers), it is certainly not the case for  $^1\text{H}$  NMR analysis of ambient aerosols.  $^1\text{H}$  NMR spectra of aerosol water-extracts containing less than 100  $\mu\text{g}$  of carbon (sample loadings reached even in remote areas) can be easily recorded at 600 MHz. Typical detection limits for individual compound H-NMR analysis are in the sub-ng  $\text{m}^{-3}$  levels (for time-integrated samplings of 12 – 24 h) thus not inferior to that of standard gas chromatography (GC)/MS or liquid chromatography (LC)/MS methods.<sup>81a</sup> The real limitations of NMR with respect to alternative off-line chemical methods consist in: (i) the complexity of the spectra for compounds with extensive J-couplings, (ii) the difficulty to acquire a second dimension, (iii) the difficulty of hyphenation with other spectroscopic and chromatographic techniques, and (iv) limited automaticity preventing the analysis of large number of samples. A further caveat specific to atmospheric applications is the lack of NMR spectra libraries for atmospheric markers. This is a major limitation because the critical step when investigating atmospheric organic compounds by  $^1\text{H}$  NMR spectroscopy is the spectral analysis and compound identification. Table 3 provides a compilation of research papers reporting chemical shift data for compounds of atmospheric importance. The vast majority of these studies were

published in the last five years, indicating that the use of NMR tools for atmospheric organic speciation is rapidly expanding.

An area of atmospheric chemistry where NMR tools have gained the widest application are the kinetic and mechanistic studies in aqueous media. The systems studied include the oligomerization of carbonyls and carboxylic acids,<sup>33,71</sup> condensation between carbonyls and ammonia or amines,<sup>72</sup> oxidation of phenolic compounds,<sup>73</sup> hydrolysis of organosulfates and organo-nitrates,<sup>74</sup> hydrolysis of epoxides,<sup>75</sup> and photochemistry of carbonyls and carboxylic acids.<sup>76</sup> NMR spectroscopy has however been less applied to the investigation of the composition of SOA produced in reaction chambers.<sup>47</sup> This is due to the complexity of these samples,<sup>72b,77</sup> the lack of chemical shift libraries and the relative small amounts of sample produced in such experiments under atmospherically relevant concentrations. But the development of continuous SOA production methods in chambers will certainly allow the application of highly informative off-line techniques such as multidimensional NMR methods in the near future.<sup>47,78</sup>

**Table 3.** Published chemical shift data for compounds of atmospheric importance.

<b>Chemical compounds or chemical classes</b>	<b>References</b>
pinonaldehyde	79
ketoaldehydes from monoterpenes	47,80
organic acids from $\alpha$ -pinene oxidation	47,81
<i>cis</i> -pinonic photo-oxidation products	76
$\alpha$ -pinene epoxide, isoprene epoxide reaction products	75a-75c
sesquiterpene oxidation products	43
tetrols and methyl-tetrols	32b,75d
methyl-glyceric acid	33
organic acids from toluene oxidation	82
chemical condensation products between glyoxal and NH <sub>3</sub>	72a
hydroxyl-carboxylic sulphate esters	74a
hydroxyl-alkyl nitrates	83

guaiacol oxidation products	84
oleic acid oxidation products	85
PAH oxidation products	86

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Some examples of successful molecular identification in ambient aerosols using NMR methods can be found in the recent literature. They include the identification of low-MW compounds such as dimethylamine, diethylamine, methanesulfonate and hydroxyl-methane-sulfonate,<sup>87</sup> as well as some major C<sub>6</sub>-C<sub>10</sub> compounds: formate, pinonic and pinic acid, and levoglucosan.<sup>88</sup> Other studies focus mainly on functional group analysis.<sup>89</sup> Interestingly, the resolution of mono- and bi-dimensional <sup>1</sup>H NMR spectroscopy allows to identify spectral fingerprints characteristic of specific chemical classes, such as aliphatic compounds carrying linear methylenic chains.<sup>90</sup>

#### **4.1.2. Mass spectrometric techniques**

##### **a) Mass spectrometry – key characteristics**

The principle of mass spectrometric techniques is to analyze compounds of interest (or analytes) based on the ions they produce. These techniques thus involve three main components: an ionization technique, a mass analyzer, and a detector. While the detectors are fairly common to all mass spectrometers, a wide range of techniques is now available for ionization and mass analysis, each of them being affected by a number of parameters. These different techniques and parameters determine the performance of a mass spectrometer and the classes of compounds that can be analyzed.

##### **Ionization methods**

This first section presents the different ionization techniques available for analytes. Over the last decades a large number of ionization techniques have been developed for organic compounds,

each of them having specific advantages and drawbacks. Only the most frequently used in atmospheric sciences are discussed in this section.

One of the most widely used ionization techniques is electron ionization (EI), which consists in colliding the analytes with 70 eV electrons. Such energetic collisions ensure the ionization of nearly all organics. It also mostly leads to fragmentation,<sup>91,92</sup> which provides structural information on single analytes, for instance, after separation from a mixture with a chromatographic system. However, the interpretation of fragmentation patterns obtained with EI becomes challenging or even impossible for complex mixtures that are not subjected to prior separation. Another energetic ionization (or “hard ionization”) method is laser desorption/ionization (LDI),<sup>91-92</sup> which suffers from the same limitations for the analysis of complex samples. Thus, the identification power of MS techniques using hard ionization such as EI or LDI, when used alone, is generally low and the *I* factor correspondingly large. However, this identification power can be very high (*I* factor close to 1), when combined with chromatographic separation (Sections 4.1 and 4.2), because the mass spectra obtained are specific and reproducible, thus can serve as fingerprints for the identification of unknown compounds, and comparable with the spectra of known compounds from a library database.

By contrast, soft ionization techniques result in much less fragmentation of the analyte, thus significantly increasing the potential of identification of individual compounds, and thus the *I* factor, in complex mixtures. However soft ionization techniques, while having relatively high ionization efficiencies, often suffer from poor sensitivity due to signal loss resulting from the transfer of the ions from ambient pressure into the vacuum system. Chemical ionization (CI) is a relatively soft ionization technique where the analytes are ionized by reaction with specific reagent ions to produce diagnostic ions.<sup>91-92</sup> Both reagent and diagnostic ions are then detected by the mass

spectrometer. Vacuum and atmospheric pressure CI (atmospheric pressure chemical ionization, APCI) are today frequently used in atmospheric mass spectrometry and on-line sampling techniques have been developed for both.<sup>93,94</sup> Another type of soft ionization technique uses a light source (photoionization, PI), for instance in the UV or vacuum UV (VUV) range, the wavelength of which can be optimized.<sup>95</sup> Such ionization technique can also be applied in the vacuum region of the spectrometer or at ambient pressure (APPI).<sup>96,97</sup> Electrospray Ionization (ESI) is another frequently-used ionization technique for atmospheric samples.<sup>91-92</sup> It has the advantage of being very soft but is only efficient for fairly polar compounds. Another drawback is that the ionization efficiencies, and thus peak intensities, of various compounds in complex mixtures vary strongly with sample composition and ionization conditions, so that ESI mass spectra are generally not representative of the overall sample composition. Beside conventional ESI analysis, a number of ESI techniques have successfully combined the sample work-up and ionization of atmospheric samples in recent years, such as desorption electrospray ionization (DESI),<sup>98</sup> nano-DESI<sup>99</sup> and liquid extraction surface analysis.<sup>100</sup> They allow organic aerosol samples to be extracted and analyzed directly from filters or impactor plate without time-consuming sample extraction.<sup>99,101</sup> Extractive electrospray ionization,<sup>102</sup> where a continuous aerosol flow is combined with an extraction solvent electrospray within the ionization source, has recently been shown to be quantitative for on-line organic aerosol analysis.<sup>103</sup>

In general, neither soft nor hard ionization techniques can reach *I* factors better than 10 when employed alone. Achieving a low *I* factor with these techniques requires to combine them with chromatographic separation (Chapter 4.2).

### **Resolution, accuracy, and dynamic range**



This section discusses the factors affecting the mass filtration and detection in mass spectrometry. Three parameters characterize the performance of mass filtration and the ability of an instrument to analyze highly complex mixtures: mass resolution, mass accuracy, and dynamic range. The resolution of an instrument is defined as the ability to resolve neighboring mass spectral peaks (Eq. 1):

$$R = (m/z) / \text{peak width at half maximum} \quad (\text{Eq. 1})$$

where  $m/z$  is the mass-to-charge ratio of an ion.

A high mass resolution can separate two compounds with mass differences of a few milli-Dalton or less, and high-resolution mass spectrometers achieve a resolution of several 100,000's (Section 4.2.3 f) for ultra-high resolutions techniques). This is especially relevant for the analysis of atmospheric aerosols where several hundred or thousands of mass spectral peaks are often measured over a mass range of a few 100  $m/z$ .

Mass accuracy is defined as the difference between the measured and theoretical mass, relative to the theoretical mass (Eq. 2) and is generally expressed in parts per million (ppm).

$$\Delta m/z = \left( \frac{\frac{m}{z_{\text{experimental}}} - \frac{m}{z_{\text{theoretical}}}}{\frac{m}{z_{\text{theoretical}}}} \right) * 10^6 \quad (\text{Eq. 2})$$

High-resolution mass spectrometers (Section 4.2.3 f)) achieve an accuracy in the low or sub-ppm range. High resolution and high accuracy instruments allow not only to characterize the entire complexity of atmospheric samples (which is especially important for one-dimensional techniques) but also to assign the elemental composition of all (or most) peaks observed in the mass spectrum.

Both mass resolution and mass accuracy directly affect the  $I$  factor that can be achieved with an instrument. Combined with other features such as chromatographic separation and/or tandem mass

spectrometry very low  $I$  factors approaching 1 can be reached with high resolution and high accuracy instruments

Finally, the dynamic range is defined as the range of analyte concentration over which the signal from the detector is directly proportional to this concentration. Although the dynamic range is not directly related to the identification power of an instrument, it can affect the detection of low-concentration compounds in mixtures that are dominated by highly abundant ones. For instance, if the full scan mass spectra of mixtures are dominated by very abundant species, the detection and subsequent identification of less abundant compounds is compromised. This can be overcome by increasing the resolution of the chromatographic separation, and by avoiding the co-elution of the highly-abundant and trace compounds. However resolving such problems generally requires specific strategies such as specific instrument settings and/or sample pre-treatment (e.g., the application of sample fractionation) to avoid reaching the upper limit of the dynamic range.

#### **b) Direct MS techniques for organic trace gases: PI-MS, CI-MS and PTR-MS**

Direct mass spectrometric techniques for the analysis of atmospheric gases, i.e., those applied to atmospheric samples without prior separation, are generally based on photo- or chemical ionization since, as explained in the previous section, this ionization technique can achieve small  $I$  factors under such conditions. In the absence of preparation or separation of the samples, the level of identification obtained depends mostly on the selectivity of the ion chemistry, i.e., the uniqueness of the diagnostic ion produced from a given analyte, and on the mass accuracy or MS/MS analysis of the diagnostic ions. In complex matrices such as atmospheric samples only a few organic trace gases can be reasonably identified ( $1 \leq I \leq 5$ ). However, direct CI-MS was primarily designed to carry out fast measurements (0.1 – 1.0 s time resolution), to study, for example, transport processes or detect highly reactive species (e.g., hydroxyhydroperoxides).

Atmospheric applications of direct CI-MS were pioneered in the mid-1980s.<sup>104</sup> The main direct CI-MS techniques currently used for the measurement of organic trace gases in the atmosphere are summarized in Table 4. The most widely used is proton-transfer-reaction mass spectrometry,<sup>105</sup> where nearly all the organic gases present in air samples are ionized by accepting a proton from hydronium ions ( $\text{H}_3\text{O}^+$ ). While the protonated diagnostic ions are fairly specific to their parent analytes all PTR-MS instruments are somewhat prone to interferences from dissociative proton or electron transfer reactions, thus to some degree of fragmentation. Early PTR-MS instruments used quadrupole filters for mass analysis, resulting in poor identification capabilities. Numerous intercomparisons with other analytical methods have shown that 10 – 15 organic gases could be detected by quadrupole CI-MS in the atmosphere without major interferences,<sup>106</sup> although their identification is not made by the quadrupole PTR-MS instrument alone but based on previous studies and plausibility arguments (the presence of only C, H, O and N atoms in the molecules).

**Table 4.** Overview of the main direct CI-MS techniques currently used for organic trace measurements in the atmosphere. Acronyms (except those in the list of abbreviations): QIT: quadrupole ion trap; LIT: linear ion trap; CIT: California Institute of Technology; TQ: triple quadrupole; LR: low resolution; NI: negative ion; PT: proton transfer; TD: thermal desorption.

Acronym	CI reagent ion	Analytes	Diagnostic ion	MS
PTR-MS	$\text{H}_3\text{O}^+$	alkenes, alcohols, carbonyls, aromatics, acetonitrile	$[\text{A}+\text{H}]^+$	Q, HR-TOF, QIT, LIT
CIT-CIMS	$\text{CF}_3\text{O}^-$	organic hydroperoxides, carboxylic acids, multifunctional organic compounds	$[\text{CF}_3\text{O}+\text{A}]^-$ $[\text{A}+\text{F}]^-$	Q, TQ, LR-TOF
NI-PT-CIMS	$\text{CH}_3\text{C}(\text{O})\text{O}^-$	carboxylic acids	$[\text{A}-\text{H}]^-$	Q

TD-CIMS	$I^-$	peroxyacyl nitrates	$[A-NO_3]^-$	Q
CIMS	$C_2H_5OHH^+$	ammonia, amines	$[A-C_2H_5OHH]^+$	Q

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These compounds include oxygenated VOCs (methanol, acetaldehyde, acetone/propanal), biogenic VOCs (isoprene, methyl vinyl ketone/methacrolein, sum of monoterpene isomers), aromatics (benzene, toluene, sum of xylene isomers) and acetonitrile, an important atmospheric biomass burning marker. The analytical deficit of the quadrupole PTR-MS instrument has been partly overcome with the proton-transfer-reaction time-of-flight mass spectrometer, allowing for high mass resolution.<sup>107</sup> This instrument can determine the elemental composition of ions, but still under the assumption that they contain only C, H, O, and N atoms. Under this assumption, organic analytes can be identified down to the isomer level, thus with *I* factors between about 2 to 5.<sup>108</sup> Prototype PTR-MS instruments with isomer-resolving MS/MS capability (ion traps) have also been developed but have been limited to a few field studies.<sup>109,110</sup>

Direct CI-MS methods using other reagent ions have been developed to target selected classes of analytes. But since none of them involves accurate mass measurements (Time-of-Flight), the identification achieved relies on the (validated or non-validated) assumption that no interferences are present in the atmospheric matrices.

An example of direct CI-MS is the California Institute of Technology – CI-MS technique, which uses trifluoromethoxy anions,  $CF_3O^-$ , to detect organic hydroperoxides, carboxylic acids and multifunctional organic compounds.<sup>111</sup> These analytes are detected as  $CF_3O^-$  adducts by low-resolution MS. Selected isobars/isomers are distinguishable via MS/MS analysis in the triple quadrupole version of the instrument. Isomeric carboxylic acids and hydroxycarbonyls can be differentiated via isomer-specific side reactions ( $F^-$  transfer to carboxylic acids). Applications of this instrument to the atmosphere have led to the measurement of peroxyacetic acid,<sup>111</sup> formic acid,

acetic acid, propionic and peroxyacetic acid,<sup>112</sup> isoprene hydroxyhydroperoxides<sup>113</sup> and epoxydiols,<sup>114</sup> methyl hydroperoxide,<sup>115</sup> acetic acid, glycolaldehyde, and hydroxyacetone,<sup>116</sup> and multifunctional organic nitrates<sup>117</sup> including isoprene hydroxynitrates. In addition, hydroperoxyaldehydes were detected in recent field studies (J. Crounse, personal communication).

A negative-ion PTR CI mass spectrometer<sup>118</sup> using acetate ions,  $\text{CH}_3\text{C}(\text{O})\text{O}^-$ , has been developed to detect carboxylic acids via selective proton abstraction reactions. The resulting conjugate carboxylate anions,  $\text{RC}(\text{O})\text{O}^-$ , are detected by quadrupole mass spectrometry. This instrument was used to measure formic, acrylic, methacrylic, propionic and pyruvic/butyric acid in the atmosphere, the latter being isomers that cannot be resolved.<sup>119</sup>

A CIMS technique to detect ammonia using protonated ethanol or acetone ions as CI was also developed.<sup>120</sup> The same ion chemistry was further incorporated to measure amines and ammonia simultaneously, at the pptv or sub-pptv level with a time resolution less than 1 min.<sup>121</sup> A PTR CI mass spectrometer was also used to measure amines and ammonia at atmospheric concentrations.<sup>122</sup>

Thermal dissociation CI-MS<sup>123</sup> is used to measure peroxyacyl nitrates (PANs) which are formed in the atmosphere from association reactions between peroxyacyl radicals,  $\text{RC}(\text{O})\text{O}_2$ , and nitrogen dioxide,  $\text{NO}_2$ . In the thermal dissociation CI-MS instrument this reaction is reversed in a heated inlet and peroxyacyl radicals react with iodide anions,  $\text{I}^-$ , in an  $\text{O}^-$  abstraction reaction. The resulting carboxylate anions are detected by quadrupole MS or ion trap MS.<sup>124</sup> Thermal dissociation-CI-MS was originally assumed to be highly selective but recent studies suggest that carboxylate anions may also be formed via secondary proton abstraction reactions from organic acids<sup>125</sup> and via  $\text{OH}^-$  abstraction reactions from peroxyacetic acids.<sup>126</sup>

In conclusion direct CI-MS techniques are efficient for the detection of many organic gases in the atmosphere, and even their identification if coupled with high-resolution MS. Their strong advantage is the fast measurements and they are also very complementary to other techniques for the identification of organic gases such as GC/MS.

Besides CI-MS techniques PI-MS techniques were applied to the detection of organic compounds in the gas phase. Because PI is largely fragmentation-free isobaric compounds with different elemental compositions are separable if the mass resolution is sufficiently high. Isomeric compounds can even be separated by MS by tuning the PI wavelength. A relatively large number of PI-MS applications deal with on-line monitoring of pyrolysis and combustion gases. From the beginning of this century the sensitivity of jet-resonance-enhanced multiphoton ionization, which has originally been applied in emission investigations,<sup>95a</sup> has increasingly been used in ambient atmosphere applications.<sup>127</sup> Aromatic compounds were investigated in the sub-ppb range applying jet-resonance-enhanced multiphoton ionization using a time-of-flight mass spectrometer downwind of a road.<sup>128</sup>

#### **c) Direct MS techniques for aerosols: The Aerosol Mass Spectrometer (AMS)**

The Aerodyne Aerosol Mass Spectrometer (AMS) was developed for the on-line measurement of organic and inorganic components of aerosols.<sup>129</sup> The principle of the instrument is to draw particles into a vacuum chamber<sup>130</sup> and impact them on a tungsten surface (molybdenum in early versions) heated to 600 °C prior to being analyzed by 70 eV EI-MS. Most of the gas material is removed by differential pumping. As explained above, while the 70 eV EI energy implies extensive molecular fragmentation, it ensures the ionization of nearly all molecules, organic and inorganic, and the compatibility of the data with existing mass spectral databases. The mass spectrum for the aerosol sample is derived by subtracting an internal background obtained from

periodically blocking the particle beam. But as it contains contributions from both the nonrefractory particles (those evaporating on the impaction plate) and from the air that was not skimmed off, these contributions are removed by using a ‘fragmentation table’ approach, where marker peaks in the mass spectra are used to quantify these components.<sup>131</sup> For other aspects of quantification, the reader is directed to Ref.<sup>129b</sup>

### **Marker ion analysis**

Because of the two-stage desorption and ionization process the AMS mass spectral data is a quantitative, linear combination of the contributions of the various particle components. It is thus possible to gain quantitative information on the overall organic composition and contributions from various sources. One of the simplest forms of analysis is the determination of the fractional contribution of key peaks to the total organic mass concentration. Because  $m/z$  44 mainly corresponds to  $\text{CO}_2^+$  from the thermal decomposition of dicarboxylic acids and multifunctional compounds,<sup>132</sup> the fractional contribution of  $m/z$  44 can be taken as a proxy for the oxygen content of the organic fraction.<sup>133</sup> When this is compared with the fractional contribution from  $m/z$  43 ( $\text{C}_3\text{H}_7^+$  from aliphatic chains and  $\text{C}_2\text{OH}_3^+$  from alcohols, monocarboxylic acids and carbonyls) correlations with the general level of atmospheric processing of the organic material can be seen.<sup>134,135</sup> Similarly, the fractional contribution of  $m/z$  60 (associated with anhydrosugars such as levoglucosan, mannosan, and galactosan) can be used in conjunction with  $m/z$  44 to monitor the evolution of biomass burning aerosols.<sup>136</sup>

### **Multi-component analysis (MCA) and positive matrix factorization (PMF)**

Beyond bulk properties, it is also desirable to quantify the contributions of different sources to the organic aerosol mass. One of the first methods for this application used the fragment ion at  $m/z$  57 ( $\text{C}_4\text{H}_9^+$  from alkanes) and at  $m/z$  44 as the basis for deriving estimates for ‘hydrocarbon-like’

and ‘oxygenated’ organic aerosol, respectively (HOA and OOA).<sup>137</sup> These data were found to correlate well with traffic emissions and secondary sources.<sup>138</sup> A modification of this technique known as multi-component analysis allows the identification of a second component of OOA through the analysis of residuals.<sup>139</sup> These two types of OOA have been linked to SOA in various stages of atmospheric processing and with different volatilities.<sup>140</sup>

A more general approach was developed with the use of PMF,<sup>141</sup> a technique imported from source apportionment methods. Its principle is to identify a number of model contributions, or ‘factors’, to the overall mass spectrum and to decompose the latter in (weighted) linear combinations of these factors by inverting the corresponding matrix.<sup>142</sup> The model factors are obtained in separate characterizations of known sources such as biomass burning and cooking.<sup>143</sup>

While this approach gives a greater confidence in the analysis of the spectra<sup>144</sup> some cases may be difficult to resolve when a significant number of mass spectral features are in common between factors, such as cooking and exhaust particles (redundant matrix terms leading to an infinite number of solutions). Generally, the confidence on the results depends on the accuracy of the target profiles.

### **Comparison with other techniques and instrument variations**

A major advantage of the AMS and other on-line MS techniques over off-line techniques is their time resolution. While the AMS is normally operated at a resolution of minutes for ambient sampling, sub-second data can be obtained if necessary, for instance for aircraft measurements.<sup>145</sup> An additional strength lies in the quantification of the overall organic fraction rather than in the identification of specific chemical species. While some species such as methyl sulfonate,<sup>87,146</sup> PAHs,<sup>147</sup> methyl furan,<sup>148</sup> and caffeine,<sup>149</sup> are unambiguously identified based on unique ions, they are exceptions rather than the rule. Trends in specific ions can be taken as indicative of functional



groups or source types and as these signals are quantitative they can be used for a mass budget analysis. Such source quantification efforts are especially effective when combined with more compound-specific techniques. For instance, off-line two-dimensional GC (GCxGC)/MS of filter samples<sup>105</sup> to identify methyl furan at  $m/z$  82 while gas-phase PTR-MS provided evidence for isoprene oxidation, supporting its identification as a marker for SOA from isoprene.

While the initial versions of the AMS used quadrupole mass filters, a major improvement of the technique occurred by using TOF mass filters<sup>150,151</sup> and later high-resolution (HR) TOF systems.<sup>152</sup> This improved the  $\Delta m/m$  resolution to around 2000 – 4000 and allowed for the elemental analysis of the ions and the resolution of peaks with multiple contributions such as  $C_2OH_3^+$  and  $C_3H_7^+$  at  $m/z$  43. The instrument can thus generally resolve pure hydrocarbon peaks from oxygenated peaks up to around  $m/z$  100, and some nitrogen- and sulfur-containing peaks.<sup>153</sup>

High-resolution data can also be used to quantify the elemental abundance by comparing signal intensities<sup>113b</sup> of ions of different elemental compositions. The apparent abundances of elements can be biased by losses of neutral and negative fragments and positive fragments such as  $H_2O^+$  and  $CO^+$  can be confounded by interferences from other particle- and gas-phase signals, so their contributions to the overall elemental composition must be estimated based on laboratory data.<sup>154</sup> While the accuracy of this method is limited in the case of individual organic species, these inaccuracies tend to average out in aerosol samples composed of a large number of different species.<sup>113b</sup> Therefore the derived elemental ratios (O/C, H/C and N/C) and associated organic matter fractions should be seen as estimates of the ensemble, not as direct measurements of individual molecules.

In conclusion, the identification of unknown compounds with the AMS is generally achieved with very large  $I$  factors, in the range of  $>10^2$ , and is not the main strength of this technique.

Milder ionization methods than 70 eV EI have been evaluated to gain additional chemical information, such as vacuum UV (VUV) photoionization<sup>155</sup> using photons of around 10 eV energy (124 nm wavelength), and thus limiting fragmentation. However, to date, this has only been achieved with a synchrotron source and has not been applied to atmospheric sampling.

#### **d) Direct MS techniques for aerosols: single particle mass spectrometry**

Single particle mass spectrometry is similar to other on-line aerosol mass spectrometric techniques in that particles are drawn into a vacuum chamber to form a particle beam before being desorbed and analyzed on-line by MS. However, the use of a pulsed laser vaporizing individual particles allows to obtain mass spectra for individual particles.<sup>156</sup> Numerous instruments employing these principles exist, many having been custom-made at research institutes.<sup>157</sup> The most common commercial version of this instrument is the aerosol TOF mass spectrometer<sup>158</sup> (ATOFMS) from TSI Inc. but others exist such as the Livermore Instruments Inc. single particle aerosol mass spectrometer and the Aeromegt laser ablation of aerosol particles time-of-flight mass spectrometer. Examples of bespoke instruments include the particle analysis by laser mass spectrometry<sup>159</sup> instrument, the single particle laser ablation time-of-flight mass spectrometer<sup>160</sup> and the nano-aerosol mass spectrometer,<sup>161</sup> among many others.

#### **Single-step techniques**

The simplest form of operation of the instrument is combined laser desorption and ionization (LDI).<sup>162</sup> The light from a laser is used to detect the presence of a particle, which triggers the LDI laser (typically an ultraviolet excimer, e.g., ArF at 193 nm, or a frequency-quadrupled Nd:YAG at 266 nm). The particle components both desorb and ionize and the data collection by the time-of-flight mass spectrometer, either in positive and negative ion, is initiated by the laser pulse. The real-time, single-particle nature of the measurement means that it can bring unique insights into

key atmospheric processes such as nucleation<sup>163</sup> or aerosol-cloud interactions.<sup>164</sup> Also, unlike thermal vaporization, LDI allows for the study of refractory species such as oligomeric material that is difficult to analyze with other techniques.<sup>165</sup>

However the main disadvantage of the technique is that the particle components can interact during the vaporization/ionization process, known as ‘matrix effects’, and result in variable ionization efficiencies and signal intensities.<sup>166</sup> Thus, the mass spectral response of different atmospheric aerosol constituents can be highly variable. In addition the relative lack of control in the desorption and ionization processes make the identification of organic species by single-step LDI non-reproducible. Some information on functionality is retained in the mass spectral fragments<sup>167</sup> and can be used for source apportionment<sup>167b,168</sup> or the identification of organic molecules such as amines,<sup>169</sup> organosulfates,<sup>170</sup> and aromatics.<sup>171</sup> However, a more sophisticated characterization of organic compounds with LDI-MS techniques is generally not possible and their *I* factor is thus as high as for AMS, in the range of  $>10^2$ .

### **Two-step techniques**

To avoid the matrix effects of single-step LDI, the desorption and ionization processes can be separated by using two laser pulses. The first one, which can be produced by an infrared laser (e.g., CO<sub>2</sub>), evaporates the particle and generates a neutral vapor, and is rapidly followed by a second pulse from a UV laser to photo-ionize the vapors.<sup>172</sup> The obtained mass spectra are more reproducible and quantitative.<sup>173</sup> The drawbacks for atmospheric applications<sup>174</sup> are that sensitivity can be significantly reduced and that the technique is not as sensitive to refractory species as single-step LDI. This makes it generally less applicable to atmospheric aerosols and more suited for laboratory studies, which are less accessible to single-step LDI. In particular, particles can be

partially vaporized and their internal structure can be probed.<sup>175</sup> Less energetic lasers can also be used to limit the extent of fragmentation during ionization.<sup>176</sup>

The first laser can also be replaced with a heated surface, as in the Aerodyne AMS, but still using a laser or VUV lamp for photoionization.<sup>96,172b,177</sup> Although the instruments can no longer be classed as ‘single particle’ this has the benefit of reducing thermal fragmentation without impacting the ability to detect and quantify organic molecules, as in the photoionization aerosol mass spectrometer.<sup>178</sup>

Two-step single particle mass spectrometry thus provides limited data on MW and basic functionality compared to other mass spectrometric techniques due to the lack of chemical separation. However, its ability to study individual particles and their internal structure means that key aerosol processes<sup>179</sup> and molecular diffusion within particles<sup>180</sup> can be studied in ways not otherwise possible.

#### **e) Isotopic separation in aerosols**

An alternative approach to the methods discussed above to characterize the wide complexity of organic material in aerosols is isotope analysis, which can be applied to the bulk or to individual compounds. The principle is to measure the isotopic fractionation between isotopic pairs such as  $^2\text{H}/^1\text{H}$ ,  $^{13}\text{C}/^{12}\text{C}$ ,  $^{15}\text{N}/^{14}\text{N}$ ,  $^{18}\text{O}/^{16}\text{O}$ , or  $^{34}\text{S}/^{32}\text{S}$  with isotopic-ratio mass spectrometry and with high precision rather than high mass resolution.<sup>181</sup> The results are expressed as an isotopic shift relative to a reference, such as:

$$\delta^{13}\text{C} = [(^{13}\text{C}/^{12}\text{C}_{\text{sample}} - ^{13}\text{C}/^{12}\text{C}_{\text{standard}})/^{13}\text{C}/^{12}\text{C}_{\text{standard}}] \times 1000 (\text{‰}), \quad (\text{Eq. 3}).$$

For instance, for  $\delta^{13}\text{C}$  the standard reference is Pee Dee Belemnite. These isotopic shifts, or fractionation, reflect kinetic isotope effects (KIE), i.e., differences between the rates of the reactions with the heavier and lighter isotope, which are involved in a number of processes such

as volatilization, chemical reactions, and condensation (Figure 4). Thus they can reflect the degree of atmospheric processing of the organic compounds in gas or aerosol bulk or as individual compounds.<sup>181-182</sup> The identification of sources is also possible if some precursors have different isotopic compositions (see below the Section “Characterization of the bulk: source apportionment”).

### **Identification at the molecular level: characterization processes**

The identification of isotopic signals at the molecular level is often limited because isotopic-ratio MS systems are optimized towards high precision and accuracy of the isotopic signal (e.g., better than  $\pm 0.1\%$  on  $\delta^{13}\text{C}$ ) but not compound identification. The separation of individual compounds for isotopic-ratio mass spectrometry is based on chromatography techniques, i.e., GC and LC (Chapter 4.2). Because of the low natural abundance of the isotopes of interest ( $^{13}\text{C}$ ,  $^2\text{H}$ , etc.) the achievable factor  $I$  is limited by the quality of the chromatographic separation and the amount of sample available for the measurement. Hence, only major organic aerosol components have been investigated by compound-specific isotope analysis in laboratory and ambient air.

In chamber experiments stable isotope measurements are employed either to determine the signature KIE's for specific processes, to apply them later to atmospheric aerosols, or for the investigation of mechanisms and rate constants of complex reactions by adding an isotopically depleted or enriched precursor.<sup>183</sup> Thus, it was shown that progressively enriching  $\beta$ -pinene with the heavy carbon isotope increased the partitioning of its ozonolysis product, nopinone, into the aerosol phase and resulted in the enrichment of its  $\delta^{13}\text{C}$  by 2.3‰ compared to the gas.<sup>183f</sup> The KIE of  $\beta$ -pinene enrichment during this reaction was also found to have a significant temperature dependence, larger enrichment taking place at lower temperature.<sup>184</sup> An enrichment of  $\delta^{13}\text{C}$  for the unreacted oxalic acid was showed in the aqueous-phase photolysis of oxalic acid in the presence

of  $\text{H}_2\text{O}_2$  and UV,<sup>185</sup> but only in the presence of Fe species catalyzing Fenton reactions. These studies indicate that, even in laboratory, the understanding of the KIE resulting from various reactions and processes requires further investigation. In addition, the enrichment factors and KIE determined in laboratory are usually limited to specific compounds and experimental conditions, and difficult to apply to other systems.<sup>186</sup> Nevertheless, some mechanisms have been successfully elucidated using these approaches, such as the uptake of the heavy oxygen isotope into dicarboxylic acids, oxocarboxylic acids, and hydroxyketocarboxylic acids in the ozonolysis of monoterpenes in the presence of  $^{18}\text{O}$ -enriched water vapor.<sup>187</sup> These results clearly indicate a direct implication of  $\text{H}_2\text{O}$  in the ozonolysis mechanism.

The measurement of stable isotope fractionation in the atmosphere has mostly been applied to small carboxylic acids, and in combination with ion chromatography (IC) or high-performance LC (HPLC) to the separation and collection of the fractions of interest. A correlation between the  $\delta^{13}\text{C}$  of gaseous formic acid and ozone concentrations was observed in the atmosphere.<sup>188</sup> However, similar correlations for particulate-phase oxalic acid were small or insignificant, probably because of opposite isotopic shifts resulting from the gas reaction (ozonolysis producing the acids) and the aerosol formation processes. These results confirm the challenges in using quantitative compound-specific isotope analysis to investigate atmospheric aerosols and further studies are needed to assess the feasibility of this approach.

Isotope analysis has been used more frequently for source apportionment than for mechanism investigation, for instance to distinguish between continental and marine oxalate by their  $\delta^{13}\text{C}$  in size-segregated aerosols in Bermuda.<sup>189</sup> The use of both  $^{13}\text{C}$  and  $^{14}\text{C}$  isotope measurements provides more information. For instance, when applied to formic and acetic acid this analysis revealed a mainly biogenic (as opposed to anthropogenic) origin of air masses at several European

sites.<sup>190</sup> But since both chemical processing and source characteristics influence the isotopic fractionation the differentiation between these factors is often difficult.<sup>191</sup>

### **Characterization of the bulk: source apportionment**

Isotope measurements of bulk aerosol fractions are mainly dedicated to source apportionment and sometimes to the monitoring of the extent of secondary aerosol formation.<sup>182,191-192</sup> For the source apportionment of organic aerosols  $^{13}\text{C}$  is the most employed stable isotope, and has been shown to display differences between plants with C3 and C4 biochemical mechanisms of carbon fixation in photosynthesis, marine and continental organic and liquid, solid and gaseous fuels.<sup>182,193</sup> However, these differences are often small compared to the natural variability of individual sources. Thus, for the investigation of organic aerosol precursors, isotope measurements have been performed on aerosol fractions enriched with secondary material, such as WSOC or humic-like substances (HULIS).<sup>182,193b,194</sup> The apportionment is often only semi-quantitative if a single isotope is considered but can improve with a multi-isotope approach.<sup>182,193b,195</sup> Another example of apportionment is the distinction between fossil, biogenic or biomass burning sources using the long-lived radioisotope radiocarbon ( $^{14}\text{C}$ ).<sup>196</sup> In particular  $^{14}\text{C}$  provides a robust attribution between fossil and non-fossil sources.<sup>182,190,194,197</sup> For example, radiocarbon measurements of OC were compared with model results<sup>196c</sup> and showed that non-fossil OC mainly stemmed from regional biogenic SOA, primary and secondary biomass burning aerosols, and primary and secondary non-fossil urban aerosols. In combination with aerosol mass spectrometry,  $^{14}\text{C}$  analysis enables source apportionment of fossil vs. non-fossil precursors for SOA-related factors such as low-volatile and semi-volatile oxygenated organic aerosol.<sup>198</sup>

Thus the combination  $^{13}\text{C}$  and  $^{14}\text{C}$  isotopes may provide deeper insights on sources and processes, such as the simultaneous distinction between marine, continental biogenic and fossil sources or the estimation of primary and secondary sources of marine aerosols.<sup>193b</sup>

#### **4.2. Multidimensional techniques**

As pointed out in the previous sections, only a very limited number of one-dimensional techniques can achieve a satisfactory structural identification ( $I < 10$ ), and for limited classes of atmospheric organic compounds. To identify a wider range compounds or complex ones, it is often necessary to combine several techniques, including some presented above. This combination dramatically lowers the overall  $I$  factor of the analysis, to reach generally a few units ( $I \leq 5$ ).

A powerful and widely-used tool to characterize complex samples is to combine chromatographic separation techniques with sensitive and specific detectors. These approaches allow to identify compounds in complex matrices and to distinguish isobaric compounds (i.e., compounds with the same nominal but a different exact MW)<sup>199</sup> or, in some cases, even isomers that cannot be distinguished with the direct MS techniques described above. Two-dimensional chromatography, e.g., in GC or LC, can further increase the resolving power for components with similar physical chemical properties, by combining different separation mechanisms.

In this section, techniques combining chromatographic separation and a detector (e.g., mass spectrometry) or techniques involving two or more stages of gas chromatography (i.e., GC×GC) or mass spectrometry (i.e., tandem mass spectrometry) are defined as two- or multi-dimensional. The analysis of organic aerosols by GC- and LC-based methods presents several challenges because of their complexity and the occurrence of compounds spanning from non-polar to very polar compounds. Complex organic aerosols containing semi-volatile compounds have been successfully determined with GC×GC-based methods. Polar compounds containing hydroxyl, oxo



and carboxylic acid functions can be measured either with GC with prior derivatization or LC-based methods, whereas polar compounds containing sulfate groups require LC-based approaches. Details and examples of such analytical tools are given below with their achievable *I*-factors.

#### **4.2.1. Separation**

The characterization of individual aerosol constituents in highly complex mixtures at the molecular level generally requires chromatographic separation. The two most employed techniques are GC, often with prior derivatization, and HPLC. The selection of a chromatographic column is crucial in the development of a suitable analytical method and must consider the chemical and physical properties of the analytes (volatility, polarity, molecular weight, solubility, etc.). In particular, if the polarities of the stationary phase and of the analyte are similar their attractive forces are strong and result in a better retention (compound appearing late in the chromatograms). The selectivity and resolution of a column are determined by the intermolecular forces between the stationary phase and the target molecules, including Van der Waals, hydrogen bonding, and dipole-dipole interactions. Its physical parameters, such as the thickness of the stationary phase, inner diameter and length, also need to be considered. Commercially available GC columns are based on stationary phases ranging from non-polar (100% dimethyl-polysiloxanes)<sup>200</sup> to increasingly polar ones, where diphenyl groups are incorporated (e.g., 5% diphenyl/95% dimethyl-polysiloxane)<sup>201</sup> or which are functionalized (e.g., 14% cyanopropylphenyl/86% dimethyl-polysiloxanes).<sup>202</sup> Columns with highly polar phases (e.g., polyethylene glycol-based)<sup>203</sup> or specific materials, e.g., for the separation of chiral components (e.g., cyclodextrin-modified phases),<sup>39</sup> are also available.

Similar principles apply to LC analysis. However, its optimization is more flexible than for GC as not only the stationary phase but also the mobile phase of the column can be modified and is

participating in the separation process (while in GC the mobile phase only ensures the transport of the medium through the column). LC analysis can be used for any compounds soluble in a liquid phase. Many different types of separation can be achieved depending on the combination of the stationary phase and the mobile phase: polarity, hydrophobicity, electrical charge, and molecular size. The physical parameters of the column, such as its retention capacity (influenced by surface area, carbon load, pore size, volume of the packing material), size and shape of the stationary phase material, and dimensions (internal diameter, length) are also critical and need to be selected carefully.

The most commonly applied LC technique is undoubtedly reversed-phase chromatography since it enables the separation of a wide range of polar and non-polar solutes (e.g., Ref.<sup>204,205,206,207</sup>). Other techniques include variations of normal phase chromatography for highly polar species such as hydrophilic interaction liquid chromatography (HILIC),<sup>208</sup> or for specific applications such as ion exchange or size exclusion chromatography used for the characterization of HULIS.<sup>209</sup>

Choosing the appropriate chromatographic separation technique for the chemical properties of the targeted compound usually leads to a high selectivity and high level of identification. While the obtained *I*-factors can vary, separation techniques are generally expected to achieve at least  $I \leq 3$ .

#### **4.2.2. Multidimensional techniques for gas analysis (GC and GCxGC)**

GC separation is suited to any volatile organic compounds and, in combination with various detectors, has been the technique of reference to measure organic gases in the atmosphere. It remains unsurpassed by other techniques such as PTR-MS, as it allows the detection of a much wider range of compounds than those undergoing chemical ionization. In combination with

preconcentration techniques it can also reach much lower detection limits. Finally it can even be used in semi-on-line mode with measurements frequencies up to 1/5 min.

Commonly used detectors in combination with GC include the flame ionization detector (FID), often rather for quantification, the electron capture detector (ECD), sensitive to halogenated species,<sup>210</sup> the nitrogen phosphorus detector for nitrated compounds,<sup>211</sup> and a range of mass spectrometric techniques enabling more detailed structural characterization.<sup>30,34,212,213</sup>

The organic gas samples collected by the various methods described in Chapter 3 are transferred to the GC instrument via a thermal desorption or solvent extraction step. Because of the low concentration of organic gases in the atmosphere this transfer often includes an additional preconcentration or enrichment step, e.g., cryofocusing, following a protocol specific to compound classes or chemical and physical properties.

### **Derivatization**

For compounds that are not sufficiently volatile or thermally too labile to pass through the injector and/or the column, derivatization procedures can be applied to the samples prior to their analysis by GC. Derivatization consists in reacting the analyte with a derivatization reagent to produce specific compounds that can be observed by the detector, such as characteristic ions when using mass spectrometric detection.<sup>214,215</sup> Derivatization can also increase the specificity of the analysis and the level of identification of certain compounds, such as mid- and larger-chain ( $>C_{10}$ ) or multi-functionalized ones. The derivatization step often takes place prior to the transfer of the sample to the GC instrument, although post-column derivatization protocols exist. Examples of the most common derivatization reagents are summarized in Table 5. Usually, they target specific classes of compounds such as carboxylic acids, carbonyl compounds, or hydroxylated compounds. In particular the derivatization of gaseous carbonyl compounds has been of considerable interest

in atmospheric science. One of the most commonly used derivatization reagents in this field of application is *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride.

**Table 5.** Overview of derivatization reagents commonly used in GC and LC analysis. Acronyms: see list of abbreviations; additional acronym: SFE: solid-phase extraction.

Principle	Targeted compound class	Derivatization reagent	Analytical technique	Reference
Alkylation	carboxylic acid and other compounds with active hydrogen	diazomethane	GC/MS	213, 36, 216
		BF <sub>3</sub> in methanol	GC/MS	217, 218, 34
		BF <sub>3</sub> in butanol	GC/MS	219, 220, 221
		pentafluorobenzyl bromide	GC/MS SFE-LC-GC/MS	222, 223 224
		tetrabutylammonium hydroxide	GC/MS	225
Silylation	alcohols, carboxylic acids and other compounds with active hydrogens (-NH, -NH <sub>2</sub> , -SH groups)	tetramethylammonium hydroxide /tetrabutylammonium hydroxide	GC/MS	226
		bis-trimethylsilyltrifluoroacetamide /1% trimethylchlorosilane/ pyridine	GC/MS	213, 227
		<i>N</i> -methyl- <i>N</i> -trimethylsilyltrifluoroacetamide containing 1% trimethylchlorosilane	GC/MS	228, 229
		trimethylsilylimidazole	GC/MS	230, 231
Acylation	carboxylic acid and other compounds with active hydrogens (-OH, -SH, -NHR groups)	acetic anhydride /4-dimethylaminopyridine in pyridine	GC/MS	232
Oxime formation	carbonyl compounds	<i>O</i> -(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride	GC/MS	233

Principle	Targeted compound class	Derivatization reagent	Analytical technique	Reference
Hydrazone formation	carbonyl compounds	2,4-dinitrophenylhydrazine	HPLC/MS	234, 235
Oxime formation	carbonyl compounds	hydroxylamine		236
	amines	6-aminoquinolyl- <i>N</i> -hydroxysuccinimidyl carbamate / NaOH	HPLC/MS	237

This reagent enables the identification of multifunctional carbonyl compounds, such as those produced by the oxidation of isoprene, which can be then identified by MS techniques such as ion trap MS.<sup>238</sup> Other derivatization procedures used in combination with GC analysis include those for amines,<sup>239</sup> amino acids,<sup>240</sup> or more specific compounds.<sup>241</sup>

Because derivatization implies a chemical reaction it can also trigger side reactions, which can interfere with the structural assignment of the analyte. This is especially critical when investigating unknown and/or multi-functionalized compounds. In these cases, alternative approaches can be necessary such as the use of different derivatization procedures<sup>222,242</sup> on different samples in the same series, or the derivatization of different fractions of a sample that was first fractionated by flash chromatography<sup>243</sup> prior to GC/MS analysis.<sup>244</sup> More common approaches include multi-step derivatizations, which target the different hydroxyl, carboxylic acid, and/or keto- or aldehyde groups of multifunctional compounds. Generally, the carboxylic acid group(s) are esterified first to methyl esters, followed by trimethylsilylation of the non-acidic hydroxyl groups and/or an additional conversion of keto- or aldehyde-groups into oxime derivatives.<sup>245</sup> In particular, this approach has led to a better characterization of monoterpene-derived<sup>246</sup> and toluene photooxidation products.<sup>247</sup> Another approach is to combine different types of ionization techniques in the GC/MS analysis, such as electron and chemical ionization. Comparing the different types of mass spectra usually leads to a higher level of identification, chemical ionization spectra identifying mainly the molecular mass of the derivative(s).<sup>245</sup> The combination of derivatization and comprehensive mass spectral characterization is a powerful tool leading to *I* factors as low as 2.

### **On-line applications**

In the past decades methods have been developed to reduce the long times usually required for GC analysis, leading to real-time field semi-on-line instruments and enabling comparisons with

important atmospheric species such as ozone, carbon monoxide or NO<sub>x</sub>. Those include coupling of GC with real-time detection techniques, such as PTR-MS<sup>248</sup> or the direct coupling of fast extraction techniques to the analytical instrument, leading to high time-resolution.<sup>249</sup> Such fast extraction techniques include the use of supercritical CO<sub>2</sub>, which is chemically inert, has a low toxicity, and is available in high purity. Another advantage is that the critical point of CO<sub>2</sub> is easily accessible at 31.1 °C and 72.9 bar, where it behaves as a gas in surface tension and as a liquid in density. The first applications of this technique to atmospheric aerosols were reported in the 1990s.<sup>250</sup> In combination with in-situ derivatization this technique has been shown to allow the identification of poly-functionalized species such as dicarboxylic acids, oxo-acids and hydroxyl-acids in the ozonolysis of sabinene.<sup>251</sup> Other fast extraction techniques that have been directly coupled to GC and applied to bulk aerosol analysis include Curie-point pyrolysis<sup>252</sup> and other thermodesorption techniques.<sup>253</sup> For Curie point pyrolysis the sample is applied onto a foil of a ferromagnetic metal and rapidly heated by induction. When reaching its Curie-point temperature the metal becomes paramagnetic and enables a fast and controlled evaporation of the analytes into the GC instrument. This technique has been applied to e.g., PAHs,<sup>252</sup> alkanes,<sup>254</sup> and, with an additional derivatization step, organic acids.<sup>255</sup> Other thermally-assisted extraction methods<sup>256,257</sup> combined with derivatization have been described<sup>226,258</sup> and offer powerful tools for the identification of unknown compounds. In particular, a field deployable thermal desorption aerosol gas chromatograph (TAG) using both FID and MS and enabling high time-resolution for aerosol analysis has been developed.<sup>259</sup> This instrument incorporates a custom-designed inlet where the aerosols are collected and thermally desorbed into the GC column. The system is automated and allows for continuous speciated measurements of organic compounds in aerosols every hour. The



inlet has recently been modified to allow less volatile gases and particles to be measured simultaneously,<sup>260</sup> thereby allowing to study their gas-particle partitioning.

Thus, the semi-on-line GC techniques described above are valuable tools for real-time monitoring of organic compounds both in the gas and particle phases, and nicely complement other on-line techniques such as PTR-MS and AMS.

### **GCxGC**

Two-dimensional gas chromatography is a powerful tool to improve the identification of organic compounds in complex mixtures, both in the gas and in the condensed phase.<sup>261</sup> It consists in coupling two GC columns in series,<sup>262</sup> generally functioning on different separation mechanisms.<sup>263</sup> The chromatograms are usually represented with the retention times for each column in x- and y-axis, respectively, and the peak height as colored contour. GCxGC is often coupled with either a flame ionization detector (for quantification) or a mass spectrometer, usually a TOFMS instrument (for identification).<sup>264</sup> Better selectivity has been sought by using more element-specific detectors such as a nitrogen chemiluminescence detector<sup>265</sup> and a nitrogen phosphorus detector, which have been applied to 15 organic nitrogen species.<sup>266</sup> But while targeting specific compounds (here nitrogen-containing ones), it does not provide structural information such as that typically provided by mass spectrometry.

The better identification level compared to classical one-dimensional GC<sup>267</sup> results from the fact that fewer compounds co-elute, providing cleaner mass spectra and corresponding to a unique set of three independent variables (retention time 1, retention time 2 and mass spectrum). This technique thus has the potential for full identification ( $I = 1$ ) but can also provide useful partial structural information using the structured nature of the chromatograms, where isomers, such as linear and branched alkanes, are grouped together. The first GCxGC analysis of VOCs in air was

performed with a flame ionization detector and showed that much of the hydrocarbon loading in an urban atmosphere was unaccounted for using conventional one-dimensional GC-FID techniques as many species at low concentrations co-elute to form a raised baseline. Later studies reported the mono-aromatic composition of gasoline, gasoline vapors and urban air samples using GC×GC-FID with a simple cooled loop injection and that many of the larger aromatic species present in gasoline vapor were also present in urban air. A total of 147 mono-aromatic isomers were isolated from a polluted urban air sample and were calculated to be a potentially significant source of tropospheric ozone. GC×GC has subsequently been used in a range of studies of atmospheric composition at locations with different sources and degrees of aging.

In spite of all these examples the use of GC×GC by the atmospheric community as a routine instrument has been slow, in part due to difficulties with quantification and because the large number of species that can be separated creates data handling problems.

#### **4.2.3. Multidimensional techniques for aerosol analysis**

##### **a) GC-ECD and GC/MS**

A large part of the GC techniques discussed in the previous section also apply to the analysis of aerosols, in particular GC×GC. Initial studies of organic aerosols by GC×GC resulted in the separation of over 10,000 organic compounds including alkanes, alkenes, cycloalkanes, n-alkane acids, alkyl- and alkenyl-substituted aromatics, polar benzenes, PAHs, and oxy-PAHs.<sup>268,269</sup> The complex amount of information gained from comprehensive techniques is associated with difficult and time-consuming data analysis. Recently profiling of complex aerosol samples has been done applying advanced scripting methods based on properties of the mass spectra.<sup>270</sup> Important areas of application of GC×GC are the identification of chemical markers and oxidized products, as the oxidized material can be separated from the rest of the sample by using a polar second column,

such as 50% phenyl polysilphenylene siloxane or polyethylene glycol columns. New oxidation products and pathways have been identified by this technique in chamber experiments. This technique has also proven very efficient for the analysis of atmospheric samples, with over 100 oxidized species observed, many linked to aromatic precursors, in filter samples from a roadside in London.<sup>271</sup> Similarly, over 50 organic compounds including oxygenated monoterpenes and previously unknown oxidation products of  $\alpha$ -pinene were identified in organic aerosols from a coniferous forest in Finland.<sup>272</sup> Oxidation products of naphthalene and phenanthrene were also identified in PM<sub>2.5</sub> samples from Seoul, South Korea.<sup>273</sup> GCxGC has also been used to identify markers for primary sources such as manufacturing processes<sup>274</sup> (Figure 5) and wood combustion,<sup>275</sup> and for the size-resolved analysis of particles collected by a differential mobility analyzer in a boreal forest in Finland, evidencing less compounds but higher proportion of hydrocarbons, aldehydes, halogenated and nitrogenated compounds in smaller particles (30 nm) than in larger ones (50 nm).<sup>276</sup>

In addition to the laboratory instruments described above two-dimensional GC $\times$ GC 2D-TAG,<sup>277</sup> for instance with a TOFMS detector,<sup>278</sup> can provide mass spectral data with high time-resolution based on the same principle. If authentic standards or mass spectral libraries are available this instrument can provide full identification ( $I = 1$ ) of organic aerosol components while enabling the investigation of time-dependent processes such as sources, aerosol aging and correlations with important atmospheric species such as VOCs, ozone, carbon monoxide, and NO<sub>x</sub>.<sup>279</sup> Other advantages of this instrument have been demonstrated in laboratory, such as information on the volatility and extent of aerosol oxidation during sesquiterpene ozonolysis, without identifying individual species.<sup>280</sup>

#### **b) IC and IC/MS**

Ion chromatography was developed already in the 70's and is still the leading analytical technique for trace analysis of ionic compounds, both inorganic and organic ones, in all types of environmental samples. As it offers a simple, reliable and inexpensive separation and determination for organic ions in complex mixtures it is also usually the first choice for the determination of low-MW organic acids in atmospheric aerosols and aqueous (cloud, fog, rain) samples.

The prerequisite that the analyte produces water-soluble ions makes of IC a rather selective analytical technique. Ion chromatography is based on two possible separation mechanisms, ion exchange and ion exclusion. The former is typically used for polar organic compounds such as low-MW dicarboxylic acids,<sup>281</sup> while the latter is generally applied to less polar organics such as weak acids.<sup>282,283</sup> Early versions of IC instruments were coupled with UV detectors,<sup>284</sup> while nowadays conductivity detectors are mostly employed.<sup>285</sup> For special applications, such as atmospherically-relevant carbohydrates (sugar alcohols, monosaccharides and monosaccharide anhydrides), high-performance anion exchange chromatography coupled to pulsed amperometric detection can be used.<sup>286</sup>

Ion chromatography can be used off-line or semi-on-line. In off-line configurations the particulate samples, collected on filters or cascade impactor foils, are first extracted in water, filtered and then injected onto the IC column.<sup>253</sup> In semi-on-line configurations the sampling system is directly connected to the IC instrument and allows for the real-time detection of organic compounds. Examples of such semi-on-line sampling systems include particle-into-liquid sampler (PILS),<sup>287,288,289,290,291</sup> wet effluent diffusion denuder/aerosol collector<sup>292,293</sup> and ambient ion monitor-ion chromatography system.<sup>294</sup>

The atmospheric organic compounds identified by IC include water-soluble low-MW organic acids present in atmospheric aerosols, the most common being monocarboxylic (i.e., formic, acetic, pyruvic and glyoxylic acids), dicarboxylic (i.e., oxalic, succinic, fumaric, malic, tartaric, glutaric, maleic, malonic,  $\alpha$ -ketoglutaric and oxaloacetic acids) and tricarboxylic acids (i.e., citric and *cis*-aconitic acids).<sup>281,285,293,295</sup> Some aromatic acids (i.e., phthalic, syringic, 3-hydroxybenzoic, 4-hydroxybenzoic, vanillic and isovanillic acid) have also been identified in aerosol particles from smoke samples,<sup>253</sup> and methanesulfonic and methanesulfinic acids both in ambient aerosols and in chamber studies.<sup>296,297</sup> More recently IC has been applied to the detection of saccharide markers in biomass burning aerosols, such levoglucosan, mannosan and galactosan, in pollen, such as inositol, glucose, galactose and fructose, and in fungal spores, such as erythritol, arabitol, and mannitol.<sup>286,298</sup> IC has also been used for the detection of aliphatic amines such as methyl-, dimethyl-, trimethyl-, ethyl-, diethyl- and triethylamine,<sup>294,296,299,300,301</sup> although the column used (Dionex CS-17) did not allow the separation of trimethyl- and dimethylamines.<sup>294</sup>

Examples of on-going and promising further applications of IC include its coupling with electrospray ionization high-resolution mass spectrometry allowing the identification of polar ionizable organic compounds that are otherwise difficult to determine by LC/MS.<sup>302,303</sup> This type of coupling, combining the high selectivity of IC with the structural identification potential of MS, is very promising for the full identification of low-MW carboxylic acids,<sup>304</sup> as the IC separation would reduce the number of eluting compounds, thus facilitating the interpretation of the mass spectra, and enabling the MS differentiation of co-eluting compounds.

However, there was only a few attempt to couple IC with MS, especially in atmospheric science.<sup>292,305</sup> Examples include the determination of the total anionic composition of urban ambient aerosols.<sup>306</sup> Although this approach leads to the identification of more than ten organic

acids (e.g., glycolic, acetic, lactic, formic, methanesulfonic, pyruvic, malic, malonic, oxalic, *o*-phthalic) with a AS-15 column and two co-eluting ones (malic and succinic), with an ICE-AS6 column several peaks remained unknown and many more compounds, mostly organic acids, unresolved. IC/MS coupling was also used for the identification of organic acids in the gas and in aerosols during the photooxidation of trimethylbenzene and propene in smog chamber experiments. The sampling was made with a wet effluent diffusion denuder/aerosol collector connected to the IC.<sup>292</sup> The fractions collected after IC separation (on a AS11-HC column) were analyzed by APCI-MS using a quadrupole mass analyzer with atmospheric pressure ionization for the identification of unresolved organic acids. Series of mono- and di-carboxylic acids, i.e., from formic to citric acid ( $I = 1$ ), were thus unambiguously identified and the MW of a number of unknown compounds up to 234 were determined.

Recently, another coupling approach of IC and ESI-MS was successfully applied to the analysis of reaction products (pyruvic, succinic, malonic, oxalic, mesoxalic acid) in the oxidation of methylglyoxal (Figure 6) and acetic acid,<sup>305a,307</sup> and in the photochemical aging of isoprene SOA in aqueous phase.<sup>305b</sup> Equipping the IC instrument with a membrane ion suppressor (e.g., ASRS-ultra suppressor operated in external water mode) eliminated the sodium ions from the mobile phase and increased the sensitivity of the MS detection by avoiding the formation of uncharged species in the interface.<sup>308</sup> Other set-ups are based on the combination of IC, ESI-MS<sup>305b,308</sup> and UV detection.<sup>302,303</sup>

### c) CE/MS

Capillary electrophoresis is an alternative to GC or LC as its separation is based on different principles and is more efficient. To be detected by this technique the analyte must be ionizable as the separation is achieved by a strong electrical field and the resulting retention times depend on

the electrophoretic mobilities of the compounds. With this technique both inorganic and organic ions, such as carboxylic acids,<sup>252,309,310</sup> can be separated in a single run. Other advantages, especially for atmospheric applications, include the requirement of only small sample amounts, such as a single drop of rain or fog,<sup>311</sup> the broad linear detection range, and the absence of extensive sample preparation, even for complex compounds such as HULIS.<sup>312,313</sup> CE is usually coupled with UV-Vis<sup>310,311</sup> or conductivity detectors,<sup>314</sup> but coupling with MS has also been performed.<sup>315,316,317,318,319,320,321</sup> However, the buffers used in CE separation can interfere with the MS ionization process and the use of sheath liquid can lead to a loss of MS sensitivity. The second problem could be avoided by coupling CE to nanospray interfaces. Examples of coupling of CE with high-resolution MS<sup>315</sup> or MS<sup>2</sup> have been reported<sup>320</sup> and should lead to the identification of unknown compounds with low *I*-factors (<5).

Taking advantage of the small amounts of sample required, several miniaturizations of this technique have been developed for the purpose of field applications and semi-online analysis. Those include the usage of microchip CE analysis<sup>322,323</sup> and coupling to PILS samplers,<sup>324</sup> which are promising approaches for routine analysis in the field. However, no structural characterization of organic aerosol components has been reported from these applications so far.

#### **d) LC-UV and LC/NMR**

While, as discussed in Section 4.1, UV-Vis spectroscopy is not specific and provides mostly bond/functional group identification (*I* ≥ 100) its coupling to liquid chromatography greatly improves the level of identification by adding information on retention times and the possibility to compare with reference standards. One of the early important applications of HPLC-UV-Vis to organic aerosols is the determination of toxic compounds such as PAHs, which are naturally strong

UV chromophores due to their aromatic structure. But this application has progressively fallen out of favor because of its poorer sensitivity compared with GC/MS methods.

In addition to separation, derivatization can enable the detection of compounds that are not natural chromophores, and be very selective, resulting in  $I \leq 10$ , by targeting specific functional groups. Numerous methodologies for HPLC/UV-Vis analysis with prior- or post-column derivatization have thus been developed and a number of selective derivatizing agents for carbonyl, hydroxyl, carboxyl or ester groups can be used. The most common derivatizing agent for carbonyl compounds (aldehydes and ketones) is 2,4-dinitrophenylhydrazine, which has been extensively used for their off-line determination in gas- and particulate-phase atmospheric samples.<sup>325,326,327,328</sup> The studies of ambient samples show that the detection limits of this technique are comparable to those of derivatization-GC/MS methods.<sup>329</sup> The organic compounds identified in atmospheric aerosols by this method span from low-MW carbonyl compounds, such as formaldehyde and acetone, to heavier compounds such as pinonaldehyde and substituted benzaldehydes.<sup>330</sup> Further optimizations of this method include additional clean up procedures and coupling with tandem MS detection. The latter enhanced the selectivity (via multiple reaction monitoring) of the detection of the  $\alpha$ -dicarbonyls glyoxal and methylglyoxal in ambient aerosol samples.<sup>331,234</sup>

Other atmospherically-relevant classes of compounds that can be selectively detected by UV-Vis spectroscopy include organic peroxides and nitrates. For instance, a thermal desorption particle beam mass spectrometer and HPLC/UV-Vis detection at 210 nm was used for the identification and quantification of organic nitrates in particulate samples.<sup>332,83b</sup> This method is interesting because organic nitrates play important roles in atmospheric chemistry but have been little studied because of the lack of suitable detection methods and standards. The method is very selective and



sensitive for alkyl nitrates since their molar absorptivity at this wavelength is much higher than that of alcohols, ketones, carboxylic acids, or alkenes.

Finally, HPLC/UV-Vis coupled with MS detection is particularly attractive for the characterization of light-absorbing organic compounds in aerosols (brown carbon) as it allows to target a subset of compounds absorbing at specific wavelengths. This approach has been recently used in the study of nitrogen-containing compounds with chromophoric properties such as nitroaromatics and imidazoles.<sup>333,44</sup> But the level of identification in complex mixtures remains low and coupling high resolution MS with HPLC/UV-Vis detection is necessary to increase it.<sup>80</sup>

### **LC/NMR**

On-line coupling between LC and NMR was introduced for the first time in the early eighties but, although it is a powerful technique for the structural characterization of organics, its applications remain scarce compared to other LC-couplings because of the low NMR sensitivity and its high costs. However, the recent development of superconducting magnets, new probe technology (especially cryogenic probes), and efficient methods for solvent suppression have remarkably improved NMR sensitivity and encouraged its application in many fields. Beside numerous publications in pharmaceutical and food science, it has been recently applied to the investigation of the chemical composition of organic compounds in aerosols, where it can be used for the structural characterization of unknown compounds. Semi-preparative LC was used to isolate a series of nitro-aromatic compounds, 4-nitroguaiacol, 6-nitroguaiacol and 4,6-dinitroguaiacol, produced by the aqueous-phase photolysis of 2-methoxyphenol, which were structurally identified by <sup>1</sup>H-, <sup>13</sup>C- and 2D-NMR, and ESI-MS<sup>2</sup>.<sup>334</sup> These compounds were then collected and used as references for comparison with ambient aerosol samples. Reference compounds for biogenic secondary products were also recently produced by a similar approach:

semi-preparative HPLC/UV-Vis was used to obtain milligrams of pure pinonaldehyde and ketolimononaldehyde in the low-temperature ozonolysis of  $\alpha$ -pinene and limonene in dichloromethane.<sup>80</sup> The isolated products were then characterized by <sup>1</sup>H-NMR spectroscopy and high-resolution MS. Recently, the use of NMR for the quantification of SOA markers produced in laboratory was further exploited by isolating them by semi-preparative LC at sub-milligram levels.<sup>47</sup>

Thus, the use of preparative LC coupled to NMR analysis can offer a high identification level, with *I*-factors = 1, but as a relatively high amount of a pure sample (ca. 10  $\mu$ g) is required this approach is limited to the most abundant species in aerosol.

#### **e) LC/MS and 2D-LC/MS**

LC/MS is one of the most robust analytical methods for the chemical characterization and quantification of highly and moderately polar organic analytes. In contrast to GC/MS methods where the critical factor for separation is the vapor pressure or boiling point of the analyte, LC separation is typically driven by the polarity strength of the individual component of the mixture. Since oxygenated organic compounds are abundant in atmospheric aerosols,<sup>140</sup> LC/MS provides an interesting method to investigate the chemical composition and changes of these polar organic aerosol components.

The reliability of the data obtained from LC/MS analysis depends strongly upon sample preparation and operating conditions. An important factor is to select the least destructive solvent for the analyte extraction. The use of polar solvents such as acetonitrile, water and a mixture of tetrahydrofuran/water, which are compatible with ESI are highly recommended. However, for certain organic mixtures, such as isoprene-derived SOA constituents, methanol was found to be the most efficient for filter extraction.<sup>335</sup> It has thus been widely used for the extraction of these

and other polar organic constituents from filters.<sup>31,36,204,335-336</sup> But potentially detrimental features of this solvent have been recently evidenced by the loss of some carboxylic acids, such as terpenoic acids, probably by reaction between the solvent and the analytes.<sup>337</sup>

In laboratory, LC/MS techniques have been used to investigate SOA formation and aging in from a range of precursors,<sup>187,335-336,338</sup> including glyoxal,<sup>339</sup> methylglyoxal<sup>305a,307</sup> methyl vinyl ketone,<sup>340</sup> glycolaldehyde,<sup>341</sup> and acetic acid.<sup>307</sup> LC/MS techniques have also been critical to identify organosulfates and their nitrated derivatives (nitrooxy organosulfates) in atmospheric samples, and reveal their large aerosol concentration.<sup>204,336d,342</sup> Prior to 2005 organosulfates were largely missed because GC/MS techniques are not able to measure them due to their low volatilities and chemical instability to derivatization.<sup>204</sup> Using LC/ESI-MS techniques in the negative ion mode provided the first molecular identification of organosulfates in coarse aerosol samples (i.e., particulate matter with an aerodynamic diameter  $\leq 10 \mu\text{m}$  (PM<sub>10</sub>)).<sup>343</sup> This work was followed by other studies performing similar analyses in PM<sub>2.5</sub> samples<sup>336c</sup> and by analyses of ambient PM<sub>2.5</sub> and laboratory-generated aerosols<sup>31,204,336d</sup> investigating the formation pathway for organosulfates in aerosols.<sup>31,336d,338c,342b,344</sup> More recently LC/ESI-MS analyses have identified organosulfates produced in laboratory experiments<sup>35b,342a,344b,345</sup> and in Arctic aerosols. However many challenges limit the application of LC/ESI-MS techniques, such as the lack of authentic standards for aromatic-derived organosulfates.<sup>346</sup> Future work should focus on synthesizing these compounds.

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#### **f) Ultra-High-resolution MS (UHRMS)**

Ultra-high resolution MS (UHRMS) is a relatively new tool for the analysis of organic aerosols, which has two important features: (i) high mass resolving power and (ii) high mass accuracy, as defined in Chapter 4.1.2. High accuracy coupled with high resolution allows determining

unambiguous elemental formulae for each ion peak, which can, in turn, be used to characterize and categorize a large number of compounds present in complex organic mixtures. The organic fraction of atmospheric aerosols often contains hundreds to thousands of species in a  $m/z$  range of 100 – 500 and, frequently, more than 10 compounds are observed within 0.1 Da, clearly illustrating the necessity of high mass resolution techniques to investigate its chemical composition.

There are three major types of high-resolution mass analyzers: the Fourier transform ion cyclotron (FTICR), the Orbitrap and the high-resolution quadrupole (Q) TOF (HR-Q-TOF). FTICR offers the best resolving power with a record resolution of 40,000,000 that was reached for reserpine at  $m/z$  609 at a magnetic field of only 7 Tesla.<sup>348</sup> Orbitrap instruments have shown to provide resolving power in excess of 1,000,000 at  $m/z$  <300 – 400 within a 3 s detection time making it compatible with several types of chromatographic separations.<sup>349</sup> Finally, HR-Q-TOF instruments have a fairly uniform resolving power of up to 40,000 across a  $m/z$  100 – 500 mass range.

Mass accuracy, on the other hand, strongly depends on various parameters including scan rate, signal-to-noise ratio, and resolving power of the instrument.<sup>92</sup> Using appropriate internal mass calibration the highest mass accuracy is generally achieved by FTICR-MS (< 0.5 ppm), followed by Orbitrap MS (1–5 ppm), and by Q-TOF MS (1–10 ppm).

The high resolving power of UHR mass spectrometers allows the characterization of thousands of organic species in a single mass spectrum by introducing the sample directly into the source without prior chromatographic separation.<sup>350</sup> This technique is generally referred to as direct infusion. A range of soft ionization techniques such as ESI,<sup>351,352,353,354</sup> atmospheric pressure photoionization,<sup>355</sup> and a variety of atmospheric pressure surface ionization methods e.g., nano-DESI<sup>356</sup> and liquid extraction surface analysis<sup>101</sup> can be coupled with UHR mass analyzers. Soft

ionization techniques allow the formation of ions with very little or no fragmentation and thus simplify the interpretation of mass spectra of highly complex mixtures.

Despite high analytical throughput of direct infusion, this method is known to be prone to matrix artifacts such as changes in the ionization efficiency of an analyte due to the presence of ‘matrix’ compounds in the mixtures. For example, sulfates, nitrates and ammonium salts are important constituents of atmospheric aerosols<sup>357</sup> and can cause ion suppression, adduct formation, and a rapid deterioration of instrument performance if injected into the ESI source.<sup>358</sup> Thus, changes in peak intensities have to be interpreted with care when comparing mass spectra of samples with different salt content or widely varying organic composition. Another limitation of direct infusion is its inability to discriminate between isomeric compounds based solely on accurate mass. In addition, non-covalent adducts (including non-covalent dimers) formed in the ESI source can lead to peaks with high  $m/z$  values, which do not reflect compounds present in the actual sample. Such potential artifacts can be minimized by varying the ionization method, the ionization voltage, or the concentration of the sample.

### **UHRMS data analysis**

Molecular formula assignment is the most critical and laborious step in HRMS analysis. Even with a mass accuracy of <1 ppm, several molecular formulas can often match a single measured mass. The number of theoretically possible assignments increases exponentially with the mass. For example, for masses of >600 Dalton (Da), more than 15 different molecular formulas can be assigned to each detected mass within a mass tolerance of 1 ppm.<sup>359</sup> Therefore, to reduce the number of matching formulae, those not likely to occur in nature are eliminated by applying a number of constraints when determining elemental formulae from the accurate mass measurements. Although various data filtering approaches are applied there are number of

essential steps which include (i) instrument error and mass drift check, (ii) restriction for the number of possible elements assumed to be present in the molecule (e.g., C, H, O, N, and S), (iii) incorporation of isotopic pattern into analysis, (iv) consideration of only chemically meaningful elemental ratios, e.g., reasonable oxygen to carbon (O/C) and hydrogen to carbon (H/C) ratios, and (v) nitrogen rule and double bond equivalent checks and additional sample specific constraints.<sup>359,4</sup>

### **Visualization methods**

Because HRMS generates very large amounts of data, their discussion and interpretation is often facilitated by visualization methods which aim to group or categorize data sets and help to identify patterns, such as differences between sampling locations or atmospheric processes in atmospheric chemistry. These visualization methods include the double bond equivalent, van Krevelen diagrams, Kendrick mass analysis and carbon oxidation state, and are described below.

#### **Double bond equivalent (DBE)**

The DBE, often referred as the index of hydrogen deficiency, is the number of double bonds and rings in a molecule. For formulae of the general type  $C_cH_hN_nO_o$ , the DBE can be calculated using Eq. 4:

$$DBE = 1 + c - 0.5h + 0.5n \quad (\text{Eq. 4})$$

where c, h and n correspond to the number of C, H and N atoms in the molecule. Other monovalent elements besides hydrogen (e.g., F, Cl, Br, I) can be counted as ‘hydrogens’, trivalent elements (e.g., P) are counted as ‘nitrogen’ and tetravalent elements (e.g., Si, Ge) can be calculated as ‘carbon’.<sup>92</sup> However, when using Eq. 4, the DBE of molecules containing elements with multiple valences (e.g., S) should be considered with caution. The DBE is useful not only for molecular assignments by eliminating molecules with unreasonable high numbers of rings and double bonds but also for comparison of the molecular composition of different environmental

samples. The data can be visualized e.g., by plotting the DBE either against the number of carbon atoms in the individual formula or  $m/z$  ratio.<sup>360,361,362</sup> For example, aromatic hydrocarbons and their oxidized derivatives that are generally characteristic for anthropogenic emissions have relatively large DBE values ( $>5$ ) and thus can be easily identified in the large dataset. Therefore, DBE plots provide additional insights into the sources and precursors of aerosols.<sup>361,362</sup>

### **van Krevelen (VK) diagrams**

The VK diagram, in which the H/C ratio is plotted as a function of the O/C ratio for each mass and corresponding formula identified in a sample, is often used to describe the evolution of organic mixtures. The method was initially developed to study the coalification process<sup>363</sup> and is applied to categorize aerosol samples. VK diagrams can also be used to differentiate potential sources of the organic aerosols by identifying major known classes of natural and anthropogenic organic compounds as illustrated in Figure 7 (see Ref. <sup>351</sup> and references therein). In general, the most oxidized species populate the lower right part of the VK plot and the most reduced/saturated species lie on the upper left part of the diagram. Moreover, aliphatic compounds typically have high H/C ratios ( $\geq 1.5$ ) and low O/C ratios ( $\leq 0.5$ ), while aromatic hydrocarbons have low H/C ratios ( $\leq 1.0$ ) and O/C ratios ( $\leq 0.5$ ).<sup>352</sup> VK diagrams are frequently plotted as three-dimensional figures with ion signal intensities included as an additional dimension.<sup>353</sup> Ion signal intensities have been used to identify concentration ratios, but because in direct infusion ion intensities do not directly reflect the concentration of the analyte but rather its ability to ionize in the media, the interpretation of this information should be done with caution. A drawback of VK diagrams is that formulae with different atom numbers but identical atomic ratios (H/C, O/C, ...) cannot be distinguished. Thus, the complexity of samples is sometimes not well represented by VK diagrams.

### **Kendrick mass (KM) analysis**

KM analysis is typically used for both formula assignment and data visualization.<sup>351</sup> It is another useful tool to observe the composition and evolution of complex organic mixtures and is frequently used to identify compound classes.<sup>364</sup> In addition, it can be applied to identify homologous series of compounds differing only by the number of a specific base unit (e.g., a CH<sub>2</sub> group). The Kendrick mass of the CH<sub>2</sub> unit is calculated by re-normalizing the exact IUPAC mass (14.01565) of CH<sub>2</sub> to 14.00000. The KM defect is calculated from the difference between the nominal mass of the molecule and the exact KM.<sup>365</sup> A consequence of this re-normalization of the atomic mass scale is that compounds that differ only by the number of base units (e.g., CH<sub>2</sub>) have exactly the same KM defect and can thus easily be identified and grouped into a homologous series. Therefore, the molecular elucidation of one compound in a homologous series allows identification of the remaining peaks in the series. KM analyses have been used to illustrate composition differences in biomass burning particles from various wood sources and to identify potential specific marker compounds.<sup>366</sup> However, if compounds are identified only via KM defect analysis as members of a homologous series their structural similarity cannot be inferred. The elucidation of chemical structures needs to be supported by additional analytical techniques, e.g., tandem mass spectrometry, LC/MS or NMR, discussed in the previous sections.

### **Carbon oxidation state (OS<sub>C</sub>)**

O/C ratios may not accurately describe the degree of oxidation of organics because other non-oxidative processes (e.g., hydration and dehydration) can affect atomic ratios in a molecule as well.<sup>367</sup> The OS<sub>C</sub> is suggested as an alternative metric to describe the chemical composition of atmospheric aerosols. OS<sub>C</sub> is shown to be strongly linked to aerosol volatility and thus is a useful parameter to classify SOA.<sup>368</sup> The carbon oxidation state can be calculated from the following equation:



$$OS_C = -\sum_i OS_i \frac{n_i}{n_C} \quad (\text{Eq. 5})$$

where  $OS_i$  is the oxidation state associated with element  $i$ ,  $n_i/n_C$  is the molar ratio of element  $i$  to carbon.<sup>367</sup> Generally  $OS_C$  is used for molecules that do not have a multiple valence, e.g., containing C, H and O atoms only.  $OS_C$  were combined for a large number of ESI-HRMS and AMS ambient data from various sampling locations,<sup>367</sup> leading to a relationship between different aerosol classes and  $OS_C$ . For instance, semi-volatile (SV) and low-volatility (LV) OOA produced by multistep oxidation reactions have  $OS_C$  values between  $-1$  and  $+1$  with 13 or less carbon atoms ( $n_C$ ). OOA and HULIS lie between the large, reduced species ( $n_C \geq 5$ ,  $OS_C$ ,  $-1$ ) and the oxidative endpoint  $CO_2$ . Biomass burning organic aerosol (BBOA) corresponding to primary particulate matter have  $OS_C$  between  $-1.5$  and  $0$  with 7 to 21 carbon atom. HOA has lower  $OS_C < -1.5$  and higher  $n_C > 19$  atoms compared to BBOA.

Thus, HRMS offers new possibilities to characterize the complexity of atmospheric organic samples due to its ability to assign molecular formulas to the majority of the peaks measured in the sample. However, to achieve levels of unambiguous identification (i.e.,  $I$ -factor of 1-2) a coupling to a chromatographic technique, such LC for instance, is needed.

#### **g) Tandem mass spectrometry**

Tandem mass spectrometry (MS/MS or  $MS^n$ ) is widely applied to obtain structural and sequence information about organic molecules. A tutorial review of these techniques is given by Ref.<sup>369</sup> The technique is used to produce structural information about a compound by fragmenting its molecular ion inside the mass spectrometer and identifying the resulting product ions. This information can then be assembled to reconstruct the structure of the initial molecule. Tandem mass spectrometry also enables the detection of specific compounds in complex mixtures on account of their specific and characteristic fragmentation patterns. Four different types of tandem

MS experiments are possible depending on the instrumentation available, i.e., product ion scanning, precursor ion scanning, constant neutral loss scanning, and selected/multiple reaction monitoring. Of these, product ion scanning offers the highest level of molecular identification, especially if used in combination with a chromatographic technique such as LC and if an authentic standard is available. In the latter case, unambiguous identification of an organic compound can be achieved ( $I = 1$ ).

Product ion scanning is particularly useful for providing structural information on small organic molecules (MW <300) such as terpenoic acids formed upon photooxidation or ozonolysis of terpenes. The structural information includes characteristic product ions as well as neutral losses, providing not only information about functional groups but also on other structural features such as locations of functional groups. An overview of specific product ions and neutral losses that are useful for characterization of SOA products, and selected references, are provided in Table 6. As most SOA products are acidic (i.e., containing one or more carboxyl groups, a nitrate, a sulfate, a phenol, or a catechol group), Table 6 mainly contains data for product ions formed by fragmentation of deprotonated molecules. Product ion spectra have also proven to be useful to derive structural information on the monomeric units of high-MW covalent dimers and oligomers.<sup>370, 371, 335, 372, 373, 40, 374, 375</sup> Figure 8 illustrates how ion trap MS<sup>n</sup> ( $n = 2, 3$  and 4) data have been used to elucidate the structure of a prominent high-MW 358 dimer as a pinyl diaterpenyl ester, which is formed upon ozonolysis of  $\alpha$ - and  $\beta$ -pinene and is also detected in ambient fine aerosol from forested environments.<sup>40, 376, 377, 378, 362</sup>

**Table 6.** Characteristic product ions and neutral losses observed upon fragmentation of protonated or deprotonated molecules useful for molecular characterization of SOA products. Acronyms: see list of abbreviations.

Precursor ion	Neutral loss (Da)	Product ion ( <i>m/z</i> )	Structural feature	References
[M + H] <sup>+</sup>	H <sub>2</sub> O (18)		carboxyl, epoxy, keto, aldehyde, hydroxyl, and lactone groups	,39,338b
	H <sub>2</sub> O + CO (46)		carboxyl group	39
[M – H] <sup>–</sup>	CH <sub>3</sub> <sup>•</sup> (15)		aromatic methoxy group	379
	H <sub>2</sub> O (18)		hydroxyl, epoxy, keto, aldehyde, and carboxyl groups	338b, 205, 380
	H <sub>2</sub> CO (30)		hydroxymethyl group	338d, 380
	NO (30)		aromatic nitro group	379
	CH <sub>3</sub> <sup>•</sup> + OH <sup>•</sup> (32)		1,2-methyl and hydroxyl groups	39, 380
	C <sub>2</sub> H <sub>2</sub> O (42)		acetyl group	380
	CO <sub>2</sub> (44)		carboxyl and lactone groups	338b, 39, 205
	C <sub>2</sub> H <sub>4</sub> O (44)		1-hydroxyethyl group	381
	HNO <sub>2</sub> (47)		aliphatic nitrate group	336d
		NO <sub>2</sub> <sup>–</sup> (46)	aromatic nitrate group	382
	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub> (58)		carboxymethyl group	380

<hr/>			
CH <sub>3</sub> COOH (60)		acetate group	39
CO <sub>2</sub> + H <sub>2</sub> O (62)		two carboxyl groups	338b, 39
HNO <sub>3</sub> (63)		aliphatic nitrate group	335, 338d, 336d
CH <sub>3</sub> <sup>•</sup> + ONO <sub>2</sub> <sup>•</sup> (77)		1,2-methyl and nitrate groups	335, 338d
SO <sub>3</sub> (80)	HSO <sub>4</sub> <sup>-</sup> (97)	sulfate group	343, 338d, 336d, 381
	HSO <sub>3</sub> <sup>-</sup> (81)		
	O <sub>2</sub> N–OSO <sub>3</sub> <sup>-</sup> (142)	1,2-sulfate and nitrate groups	338d, 336d
<hr/>			

Furthermore, accurate mass data can be obtained not only for precursor ions but also for their product ions with high-resolution FTICR, Orbitrap, and Q-TOF instrumentation.<sup>373,374,383,338d,384,235</sup> Precursor ion and neutral loss scanning have also been employed occasionally for screening complex atmospheric aerosol samples. Precursor ion scanning has been applied to monitoring groups of compounds which fragment to common product ions, e.g., nitro-aromatic compounds resulting in  $m/z$  46 ( $\text{NO}_2^-$ ).<sup>382,385</sup> Constant neutral loss scanning has been used to monitor carboxylic acids in positive ion APCI after conversion to methyl esters, which result in loss of methanol (32 Da),<sup>386</sup> and nitro-aromatic compounds in negative ion APCI, which result in loss of NO (30 Da).<sup>382</sup>

Selected/multiple reaction monitoring is particularly useful to confirm unambiguously both the presence and identity of compounds in atmospheric samples, e.g., the detection of carboxylic acids<sup>208</sup> and of nitro-aromatic marker compounds that are specific to biomass burning.<sup>387</sup> This scanning mode is not only highly specific but also highly sensitive. Unlike for the other tandem MS experiments the targeted analyte must be known and have been well characterized previously before this type of experiment is performed.

Thus, tandem MS techniques used in combination with LC are very advanced analytical tools for both the detection and the detailed mass spectrometric characterization of organic compounds in complex atmospheric samples.

## **5. Current challenges involving atmospheric organic compounds**

This last Chapter presents specific topics in atmospheric chemistry where organic compounds are essential and important questions remain to be elucidated. The objective is both to provide examples of applications of the techniques presented above to the identification of organic compounds in different contexts and to identify some possible future applications or developments.

## **5.1. Secondary organic aerosols**

This chapter focuses on secondary organic aerosols (SOAs), which are expected to have a large contribution to ambient aerosols, air quality and pollution, climate and the biogeochemical cycles. Section 5.1.1 presents the main definitions and challenges linked to this subject. Section 5.1.2 presents the main approach to determine atmospheric SOA mass from condensable precursors (source apportionment) and summarizes the other processes expected to contribute to SOA formation and aging (condensed-phase reactions). Section 5.1.3 focuses on the molecular markers for biogenic SOA. Finally, Section 5.1.4 provides some future directions on the molecular characterization of SOA.

### **5.1.1. Terminology and background**

The terminology associated with atmospheric organic aerosol is not coherent and often leads to confusion, inconsistency, and misunderstanding.<sup>388</sup> SOA is defined as liquid or solid particles created in the atmosphere by the transformations of organic gases.<sup>389</sup> These transformations can include gas-phase oxidation followed by condensation on pre-existing atmospheric particles and/or condensed-phase reactions in or at the surface of pre-existing particles (aerosols or cloud droplets).<sup>389b</sup> By contrast, primary organic material or primary organic aerosol (POA) is condensed-phase organic material emitted directly from the ground. Because these definitions are based on processes rather than on properties of the organic compounds, they make it challenging to identify primary and secondary organic compounds directly in atmospheric aerosols. For this reason, most of the current knowledge on SOA, including their formation mechanisms, markers, or contributing multiphase reactions, is based on laboratory or smog chamber experiments and introduce many unknowns and uncertainties when extrapolated to the atmosphere. In addition, because the above definition of SOA potentially includes various formation processes, it can lead

to many different practical descriptions of atmospheric SOA and of their corresponding mass, markers, and properties. Therefore, the main challenges concerning atmospheric SOA today relate to its identification and quantification, and are illustrated by the large discrepancies between modeled and measured atmospheric SOA mass, which have been debated for nearly a decade. More recent studies have also started to tackle other challenges, such as the characterization of other SOA properties: overall composition (O/C and H/C ratios ...), optical properties, and cloud-forming properties.

The first practical description of SOA was entirely based on the smog chamber investigations of the gas-phase oxidation of various precursors in the presence of inorganic seeds, and led in the mid-90's<sup>390</sup> to the first SOA formation model: the gas-to-particle partitioning theory.<sup>391</sup> This theory, which is still today the most widely-used in atmospheric models, is based on the thermodynamic equilibrium of condensable organic compounds between the gas and the particulate phase. Initially, only limited classes of gas precursors were identified by the experiments, terpenes and aromatic compounds. Their oxidation products, to which those of isoprene were later added, thus provided the first markers for SOA and the first method to quantify them in the atmosphere by source apportionment studies (see next section).

The development and applications of the Aerodyne AMS (Section 4.1.2.c) in the 2000's led to other practical descriptions of SOA and different markers, which were also validated by smog chamber experiments. SOA were assimilated to the low- and semi-volatile oxygenated organic fractions LV-OOA and SV-OOA, respectively, corresponding to different stages of aging.<sup>140</sup> Their markers are the fragmentation patterns obtained with the same instrument for smog chamber SOA. Statistical tools such as PMF, CMB or their combination thus allowed to quantify atmospheric SOA with this instrument with high time resolution.<sup>144</sup>

However, while atmospheric models estimated SOA to represent a large, sometimes dominant, fraction of the atmospheric organic particles mass,<sup>385,393,394,392</sup> it became evident in the 2000's that they still underestimated this mass by several orders of magnitude.<sup>393</sup> A new SOA formation model was proposed to account for this missing mass: the volatility basis set (VBS).<sup>394</sup> It consists in widening the range of precursors taken into account in the gas-to-particle partitioning to all semi-volatile compounds. This introduced thus a somewhat different practical description of SOA, represented by semi-volatile markers. The adequacy of this model was demonstrated with the SOA produced by the Deepwater Horizon spill, which was mostly accounted for by the contribution of semi-volatile compounds.<sup>395</sup>

Implementing the VBS in atmospheric models succeeded in reducing some of the discrepancies between predicted SOA masses and observations, but was not sufficient in some cases, for instance for above Europe with the EMEP model.<sup>396</sup> A number of directions are currently being explored to account for these remaining differences. Recent works, using the gas-phase oxidation of  $\alpha$ -pinene as an example, indicated the important contribution of extremely low-volatility oxidation products (ELVOCs) to SOA mass, currently not taken into account in models.<sup>397</sup> In addition, over the last decade, several classes of condensed-phase reactions were identified as likely to contribute to SOA mass and properties (see next section). But they are still under investigation and their applications to atmospheric models limited, so far.

Organic identification has been key in all these developments and in most of the progress accomplished in the understanding of SOA over the past three decades. It will continue to be key in elucidating the remaining unknowns of this topic.

#### **5.1.2. Source apportionment and condensed-phase processes**



As explained above, the main criterion used so far to evaluate our understanding of atmospheric SOA has been the comparison between their modeled and measured masses. Only recently other criteria started to be considered, such as their average elemental composition (ratios O/C, H/C...),<sup>140,398</sup> now accessible with HRMS instruments such as the AMS or LC/HRMS. This section presents the main approach to estimate the atmospheric SOA mass resulting from condensable precursors, source apportionment, and summarizes the other processes currently expected to contribute to SOA mass and properties.

**Source apportionment for condensable precursors.** SOA precursors include VOCs emitted by biogenic (terrestrial and marine ecosystems) and anthropogenic sources (biomass burning, fossil fuel combustion). Globally, the biogenic precursors dominate, isoprene being expected to be the main one.<sup>399</sup> Other biogenic and anthropogenic hydrocarbons such as oxygenated biogenic compounds (1,3-butadiene, and 2-methyl-3-butene-2-ol),<sup>5,400</sup> sesquiterpenes, and aromatics, also contribute, but to a smaller extent. At local or regional scale, however, these precursors can have a significant contribution to SOA mass. Another potential source of SOA is the oxidation of evaporated POA vapors.<sup>394b</sup> The non-volatile POA from diesel exhaust and biomass burning is known to include low-volatility compounds that partition between the gas and aerosol phase. These compounds can then undergo gas-phase oxidation to form species of different volatilities that form SOA.<sup>394b,401</sup>

The identification of SOA markers in smog chamber experiments made possible the investigation of the contribution of specific precursors to atmospheric SOA.<sup>400a,400b,402</sup> However while unique chemical markers are available for primary sources such as motor vehicle exhaust, wood combustion, coal combustion, meat cooking, tobacco smoke,<sup>389b</sup> the construction of unique chemical profiles for SOA requires complex source apportionment models. Recently, several such

SOA source apportionment studies have been conducted to assess the impact of SOA in global, regional and local air quality, including a SOA molecular marker method<sup>403</sup> and the use of SOA molecular markers in CMB and other receptor models,<sup>404</sup> and for studying SOA gas-to-particle partitioning compounds,<sup>405</sup> OA aging/gas-to-particle partitioning of semi-volatile VOCs in source apportionment models (CMB and PMF),<sup>406</sup> and reactions contributing to ambient OA.<sup>377</sup>

Source apportionment in time-resolution of minutes can be achieved with the AMS technique while classical filter collection techniques provide the same information with a frequency of about a day. Using the AMS, SOA is quantified with statistical tools such as PMF, CMB or their combination.<sup>144,140</sup> These approaches require a prior classification of SOA precursor types from individual sources, as illustrated with 17 compounds for the determination of atmospheric SOA from isoprene, monoterpenes,  $\beta$ -caryophyllene, and aromatics.<sup>407</sup> However, since the quantification of these individual sources rely on laboratory studies and may vary considerably with the experimental conditions, this approach is to be applied to ambient SOA with caution. The combination of AMS and <sup>14</sup>C analysis enables a more reliable source apportionment for fossil vs. non-fossil precursors for OOA, as the <sup>14</sup>C analysis is quantitative and independent of emission factors or potential chemical transformations in the SOA. This approach was illustrated by the apportionment of a major fraction of non-fossil sources to total OOA in Zurich, and to LV-OOA and a smaller fraction to SV-OOA, respectively, in Los Angeles.<sup>198c,408</sup>

### **Condensed-phase reactions contributing to SOA**

Since the beginning of the 2000's evidence has accumulated that condensed-phase reactions contribute to SOA formation and aging. Some was obtained from atmospheric observations and other from laboratory studies. The first type of evidence is the identification in ambient aerosols of compounds clearly resulting from condensed-phase reactions. Some of the first and most

important examples were the 2-methyltetrols,<sup>5</sup> which were found in a wide range of atmospheric aerosols and identified as products of isoprene. However, their hydroxyl functional groups clearly indicated another origin than gas-phase oxidation alone, as the latter produces essentially carbonyl or acid groups. These compounds were proposed to result from the liquid-phase hydrolysis<sup>344b,409</sup> of the gas-phase epoxydiols<sup>114</sup> produced in the low-NO<sub>x</sub> (NO<sub>x</sub> = NO + NO<sub>2</sub>) atmospheric oxidation of isoprene. The reactive uptake of these epoxydiols on acidic sulfate aerosols was also demonstrated to contribute to SOA mass.<sup>344b,409a,410</sup> Another important class of compounds found in ambient aerosols and clearly resulting from condensed-phase reactions are organosulfates. As explained in Section 4.2.3, their ubiquity and abundance in atmospheric aerosols<sup>411</sup> was mostly revealed by LC/MS techniques.<sup>343,336c</sup> Their organic structures indicated that they resulted from biogenic precursors, which had undergone secondary reactions in sulfate-containing aerosols. Laboratory and smog chamber investigations have shown that these compounds were produced by the gas-phase oxidation of isoprene and terpenes followed by the reaction of the epoxy-containing products with sulfuric acid in acidic sulfate aerosols,<sup>31,204,336d,338c,342b,344</sup> thus providing a plausible formation pathway in the atmosphere. Radical mechanisms, in particular involving the sulfate radical, were also shown to produce the same compounds but at neutral pH.<sup>412</sup> The exact mechanism accounting for the large concentrations of organosulfates in ambient aerosols still remains to be determined.<sup>411</sup>

Other type of atmospheric observations indicating the contribution of condensed-phase reactions to SOA consist in mass or chemical budgets. An example was the unexpectedly low gas-phase concentration of glyoxal in the MCMA-2003 campaign in Mexico City, matching an unaccounted SOA mass, and thus indicating the formation of SOA by condensed-phase reactions of this

precursor.<sup>413</sup> The role of glyoxal as SOA precursor has been, since then, largely confirmed by laboratory and smog chamber<sup>28,414</sup> and is still under investigation (see below).

Substantial evidence that condensed-phase reactions contribute to SOA has also been obtained from laboratory and smog chamber investigations. Towards the end of the 1990's, the ionic reactions of organic compounds in atmospheric aerosols, thus in the dark but in the presence of catalysts, started to be explored.<sup>415</sup> The importance of acid catalysis for C-C bond-forming reactions such as aldol condensation,<sup>415-416</sup> and C-O-C bond-forming reactions such as acetal and oligomer formation<sup>417</sup> was studied first. These reactions received ample attention as they were shown for the first time to have large contributions to SOA mass.<sup>418</sup> This contribution was found to be due to the very large apparent Henry's law constant of the precursors in acidic media, itself resulting from their equilibrium with their many dissolved forms (protonated, enols...).<sup>416b,416d</sup> However, such large Henry's law constants, and significant reaction rates were only achieved for very large acid concentrations ( $> 50\%$  wt  $\text{H}_2\text{SO}_4 \sim 7\text{ M}$  of  $\text{H}^+$ ). Thus, while efficient to produce SOA in smog chamber, these acid-catalyzed processes were concluded to be unrealistic in tropospheric aerosols. This prompted the investigation of other catalysts enabling the same reactions, at neutral pH and other typical tropospheric conditions. Iminium catalysis met these criteria, and was first illustrated with amino acids,<sup>419</sup> then established for the first time with inorganic ammonium ions,  $\text{NH}_4^+$ ,<sup>419a,420</sup> one of the most abundant components of tropospheric aerosols. However, unlike with acid catalysis, the uptake of many precursors on neutral ammonium-containing seeds does not contribute significantly to SOA mass.<sup>414a</sup> Notable exceptions are, however, glyoxal, and to a lesser extent methylglyoxal, for which the formation of SOA on neutral ammonium seeds in the dark<sup>28,414,421</sup> and the uptake on amino-acid-containing solutions<sup>422</sup> have been demonstrated. Another interesting aspect of the reactions of carbonyl

compounds with  $\text{NH}_4^+/\text{NH}_3$  is that, in addition to the catalytic channels, they involve non-catalytic condensation channels producing C-N compounds, which strongly absorb light in the UV-Vis region. Thus, the formation of imidazoles absorbing up to 300 nm in the SOA produced by glyoxal and ammonium sulfate seeds<sup>72a,414b,423</sup> or in amino-acid or amine-containing media<sup>424</sup> was reported. More recently, the condensation of a keto-aldehyde from limonene in ammonium salt solutions was shown to produce compounds absorbing near 500 nm.<sup>80,424d,425</sup> Such condensation reactions in ammonium salts are important for the formation of brown carbon and the optical properties of SOA, and are also discussed in Chapter 5.3.

Other condensed-phase reactions than ionic ones have also been reported from SOA smog chamber experiments, such as those producing oligomers, which were identified using matrix-assisted laser desorption ionization and ESI mass spectrometry.<sup>426</sup> These reactions seem to have radical mechanisms, similar to those taking place in more diluted, aqueous media. Note that it is important to distinguish between “aqueous-phase” conditions,<sup>427</sup> in which the solute are in small concentrations (< 0.1 M) from condensed-phase or aerosol-phase conditions where inorganic salts and other compounds are at much larger concentrations (>> 1 M) and water molecules are minor.

Finally, the role of light-induced condensed-phase reactions to SOA has also been evidenced. In particular, glyoxal was shown to produce much more SOA mass in the light than in the dark.<sup>28</sup> These light-induced processes have been recently proposed to result from photosensitized reactions, where some imidazoles produced by glyoxal were found to act as efficient photosensitizers.<sup>428</sup>

All these condensed-phase reactions are still under investigation but the contribution of some of them to SOA in the atmosphere has started to be evaluated by atmospheric models. This is, in particular, the case for the reactions of glyoxal,<sup>398</sup> which were found to have a significant impact

on the average O/C ratio of the SOA.<sup>398</sup> The evaluation of the role of these reactions in atmospheric SOA would now require to identify some of their markers in atmospheric aerosols, such as the imidazoles from glyoxal or more complex condensation products with ammonium salts.

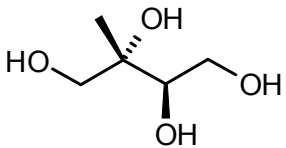
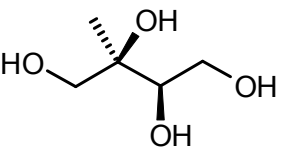
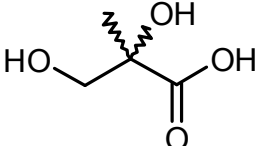
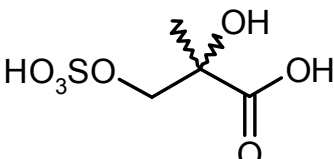
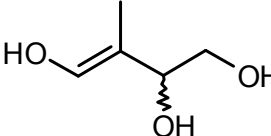
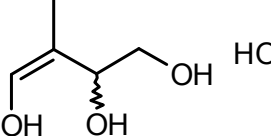
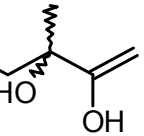
### 5.1.3. Molecular markers for biogenic SOA

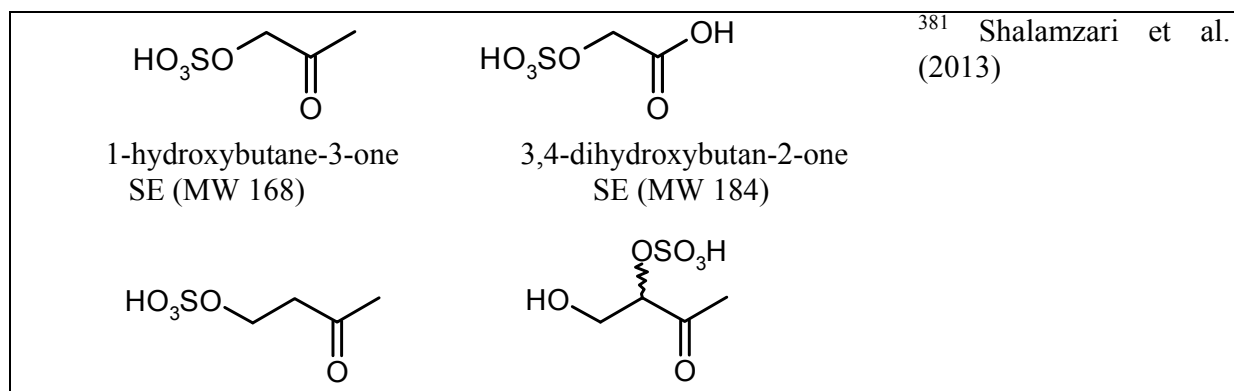
This section focuses especially on molecular markers for biogenic SOA because biogenic VOCs are the dominant precursors for SOA<sup>429</sup> and the molecular markers for anthropogenic SOA are rather well known,<sup>389b</sup> except for biomass burning SOA markers, which have more recently been characterized (Chapter 5.2).

The identification and quantification of specific molecular markers originating from SOA due to different precursors are essential towards accurate assessment of their impacts in source apportionment studies. In addition, molecular speciation provides fundamental insights into SOA source processes, i.e., the chemical reactions leading to their formation. Furthermore, molecular markers can serve as a "clock" for measuring the OA aging state. Molecular speciation activities started in the late 90's for monoterpene SOA,<sup>187,218,246,338a,370,430</sup> but started much later for isoprene SOA, i.e., after 2004 following the discovery of the 2-methyltetrols.<sup>5</sup> During the past two decades substantial progress has been made with the structural elucidation (high identification level I  $\leq$  2) of biogenic SOA markers. In this section an update will be given for markers related to isoprene and  $\alpha$ -pinene, and information for markers related to other selected BVOCs (i.e.,  $\beta$ -pinene, *d*-limonene,  $\Delta^3$ -carene, and  $\beta$ -caryophyllene) will be briefly presented.

**Isoprene SOA markers.** A compilation of isoprene SOA markers and selected references about their structural characterization are given in Table 7.

**Table 7.** Overview of isoprene SOA markers reported in the period 2004-2009 and since 2009, and selected references on their structural characterization. Abbreviation: sulfate ester, SE.

Chemical structure and name (MW)	Selected references
<i>Markers reported in the period 2004-2009 [for a more complete compilation, see Hallquist et al. <sup>389b</sup>]</i>	
<p>2-methyltetrols (MW 136) (2-methyl-1,2,3-tetrahydroxybutane)</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  <p>2-methylthreitol (2R,3R) + 2S,3R isomer</p> </div> <div style="text-align: center;">  <p>2-methylethritol (2S,3R) + 2R,3S isomer</p> </div> </div> <p>2-methyltetrol derivatives  2-methyltetrol organosulfates (MW 216)  2-methyltetrol nitrooxy organosulfates (MW 261)  2-methyltetrol dinitroxy organosulfates (MW 306)</p>	<p><sup>5</sup> Claeys et al. (2004)  <sup>431</sup> Wang et al. (2004)  <sup>335</sup> Surratt et al. (2006)</p> <p><sup>204</sup> Surratt et al. (2007)  <sup>338d</sup> Gomez-Gonzalez et al. (2008)  <sup>336d</sup> Surratt et al. (2008)</p>
<p>2-methylglyceric acid (MW 120) (2,3-dihydroxy-2-methylpropanoic acid)</p> <div style="text-align: center;">  </div> <p>2-methylglyceric acid SE (MW 200)</p> <div style="text-align: center;">  </div>	<p><sup>30</sup> Claeys et al. (2004)  <sup>335</sup> Surratt et al. (2006)  <sup>432</sup> Szmigielski et al. (2007)</p> <p><sup>338d</sup> Gomez-Gonzalez et al. (2008)</p>
<p>C<sub>5</sub>-alkene triols (MW 118)</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  </div> <div style="text-align: center;">  </div> <div style="text-align: center;">  </div> </div>	<p><sup>229</sup> Wang et al. (2005)  <sup>335</sup> Surratt et al. (2006)</p>
<i>Novel markers reported since 2009</i>	
<p>polar organosulfates related to methacrolein or methyl vinyl ketone  hydroxyacetone SE (MW 154)  glycolic acid SE (MW 156)</p>	<p><sup>74a</sup> Olson et al. (2011)  <sup>412d</sup> Schindelka et al. (2013)</p>



In recent years improved mechanistic insights have been obtained about the formation of isoprene markers under different experimental (smog chamber) conditions. As explained previously, the 2-methyltetrols, their corresponding sulfate esters and the C<sub>5</sub>-alkene triols are generated from the condensed-phase reactions of the C<sub>5</sub>-epoxydiols produced in the gas-phase photooxidation of isoprene under low-NO<sub>x</sub> conditions.<sup>410</sup> By contrast, 2-methylglyceric acid and its corresponding sulfate ester have been shown to require high-NO<sub>x</sub> conditions and methacrylic acid epoxide, formed by decomposition of methacryloylperoxynitrate, as a gas-phase intermediate.<sup>433</sup> Insights have also been gained about the formation of the 2-methyltetrols and corresponding sulfate esters under high-NO<sub>x</sub> conditions, where the oxidation of isoprene with OH radicals partly results in the formation of organonitrates, which subsequently partition to the particle phase and can undergo a nucleophilic substitution with water or sulfate.<sup>74b,434</sup> Isoprene SOA-related organosulfates that recently have been structurally elucidated and detected in ambient fine aerosol include sulfate esters of 3,4-dihydroxybutan-2-one, glycolic acid, 1-hydroxy-3-oxobutane, and hydroxyacetone.<sup>74a,381,412d,414b,435</sup> As explained in the previous section, their formation, as well as the sulfate ester of 2-methylglyceric acid, has been explained by multiphase reactions involving either sulfuric acid or the sulfate radical anion.<sup>74a,412d,414b,435</sup>



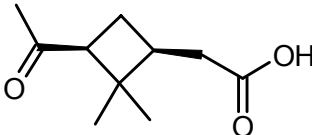
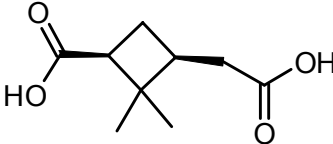
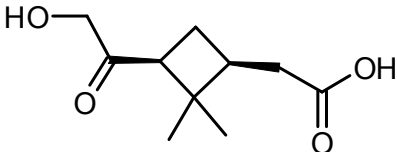
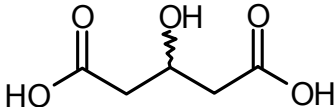
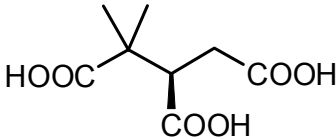
The isoprene SOA markers, the 2-methyltetrols, the C<sub>5</sub>-alkene triols and 2-methylglyceric acid have mainly been analyzed with GC/MS with prior trimethylsilylation,<sup>5,229,431</sup> whereas LC/MS methods based on (–)ESI have been applied to the analysis of isoprene SOA-related organosulfates.<sup>204,336d,338d,381,412d,435</sup> Due to their high polarity C<sub>18</sub> reversed-phase HPLC columns with polar retention have been employed, such as di- and trifunctionally-bonded phases, which do not suffer from stationary phase collapse when a mobile phase is used with a high water content (> 95%). In addition, ion-pairing reversed-phase LC/MS using dibutylammonium acetate as ion pairing reagent has been applied to polar isoprene-related organosulfates.<sup>436</sup> Quantification of isoprene SOA markers (i.e., 2-methyltetrols, C<sub>5</sub>-alkene triols, and 2-methylglyceric acid) has mainly been performed using GC/MS with prior trimethylsilylation.<sup>437</sup> However, the developed methods have not been fully validated, mainly due to the lack of sufficiently pure authentic standards (>95%) for the 2-methyltetrols and 2-methylglyceric acid, and the complete lack of authentic standards for the C<sub>5</sub>-alkene triols. With respect to the quantification of polar isoprene-related organosulfates such as 2-methyltetrol and 2-methylglyceric acid sulfate esters, methods based on LC/(–)ESI-MS have been employed.<sup>437b,438</sup> But these methods have not been validated either and suffer from shortcomings such as the lack of authentic reference standards so that surrogate compounds need to be utilized.

An isoprene SOA marker which occupies a special position is methyl furan, first detected using the AMS technique and GCxGC/MS in a field campaign in the Borneo tropical forest.<sup>148</sup> Methyl furan is not in itself present in the particles but is thought to be produced through the decomposition of isoprene epoxydiol-related SOA species such as 3-methyltetrahydrofuran-3,4-diols during the thermal desorption used in both techniques.<sup>439</sup> It is a particularly useful marker because it produces

a distinctive signal in the AMS mass spectrum at  $m/z$  82, allowing source apportionment (Section 4.1.2).

**$\alpha$ -pinene SOA markers.** A compilation of  $\alpha$ -pinene SOA markers with selected references describing their structural characterization is given in Table 8.

**Table 8.** Overview of  $\alpha$ -pinene SOA markers reported before and since 2007, and selected references on their structural characterization. Only markers that are detected at substantial concentrations ( $>10 \text{ pg m}^{-3}$ ) in ambient fine aerosol have been included. Abbreviation: sulfate ester, SE.

Chemical structure and name (MW)		Selected references
<i>Markers reported before 2007</i>		
<i>cis</i> -pinonic acid (MW 184)	<i>cis</i> -pinic acid (MW 186)	<sup>370</sup> Hoffmann et al. (1998) <sup>218</sup> Christoffersen et al. (1998) <sup>246</sup> Yu et al. (1999) <sup>338b</sup> Glasius et al. (1999) <sup>338a</sup> Larsen et al. (2001)
		
10-hydroxy- <i>cis</i> -pinonic acid (MW 200)		
<i>Markers reported since 2007</i>		
3-hydroxyglutaric acid (MW 148)		<sup>34</sup> Claeys et al. (2007)
		
3-methyl-1,2,3-butanetricarboxylic acid, MBTCA (MW 204)		<sup>36</sup> Szmigielski et al. (2007)
		
lactone-containing terpenoic acids and related marker		<sup>440</sup> Claeys et al. (2009)
terpenylic acid (MW 172)	terebic acid (MW 158)	<sup>205</sup> Yasmeeen et al. (2011)

<div data-bbox="327 302 614 481"> </div> <p>diaterpenylic acid acetate (MW 232)</p> <div data-bbox="702 302 949 481"> </div> <p>2-hydroxyterpenylic acid (MW 188)</p> <div data-bbox="311 582 646 761"> </div> <div data-bbox="726 582 997 761"> </div>	<p><sup>441</sup> Kahnt et al. (2014)</p>
<p>organosulfates and nitrooxy organosulfates</p> <p>3-hydroxyglutaric acid SE (MW 228)</p> <p>hydroxypinonic acid SE (MW 280)</p> <p>2,3-dihydroxypinane nitrooxy organosulfates (MW 295)</p> <div data-bbox="359 996 582 1176"> </div> <p>+ 2 positional isomers</p>	<p><sup>31</sup> Surratt et al. (2007)</p> <p><sup>336d</sup> Surratt et al. (2008)</p>
<p>high-MW dimers</p> <p>pinyln-hydroxypinonyl ester (MW 368)</p> <div data-bbox="255 1310 933 1556"> </div> <p>pinyln-diaterpenyl ester (MW 358)</p> <div data-bbox="255 1624 805 1915"> </div>	<p><sup>372</sup> Müller et al. (2008)</p> <p><sup>40</sup> Yasmeeen et al. (2010)</p>

Despite the fact that molecular speciation already started in the late 90's significant progress has only been made in the last decade with a more complete molecular speciation of  $\alpha$ -pinene SOA and insights into their formation processes. A marker that has received particular attention is 3-methyl-1,2,3-butanetricarboxylic acid,<sup>36</sup> which is now established as a suitable marker for aged  $\alpha$ -pinene SOA.<sup>442</sup> For an account on the discovery of MBTCA, see Ref.<sup>443</sup> Other novel markers that have structurally been characterized include 3-hydroxyglutaric acid,<sup>34</sup> the lactone-containing terpenoic acids, terpenylic acid, terebic acid, 2-hydroxyterpenylic acid, 4-hydroxyterpenylic acid, and diaterpenylic acid acetate.<sup>440-441</sup> Furthermore, high-MW dimers have received ample attention and have been structurally identified and detected in ambient fine aerosol with the two most prominent ones being diesters with MW 368 and 358.<sup>40,362,370,372,376-378</sup> The MW 368 dimer was shown to consist of a pinyl and a hydroxypinonyl monomeric unit,<sup>372</sup> while the MW 358 dimer was found to comprise a pinyl and a diaterpenyl residue.<sup>40,376</sup> They were demonstrated to be formed through ozonolysis in the gas phase and not, as previously postulated, by acid-catalyzed esterification of monomeric terpenoic acids in the particle phase,<sup>40</sup> and were speculated to involve the participation of Criegee intermediates.<sup>378</sup> The exact formation mechanism of high-MW dimers warrants further investigation as they are implied in new particle formation.<sup>370,378</sup>

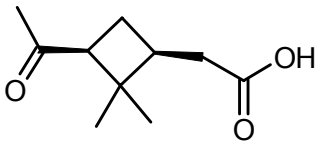
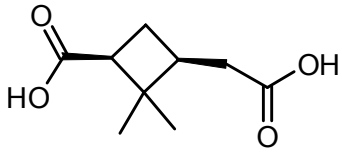
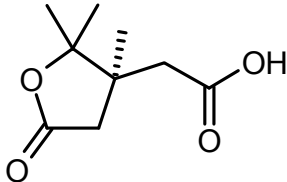
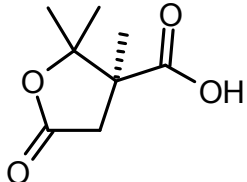
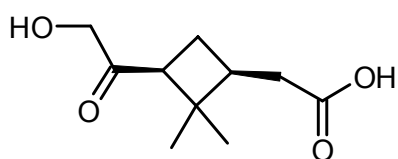
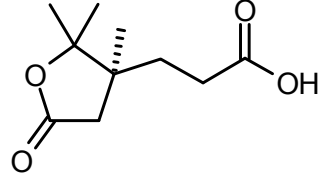
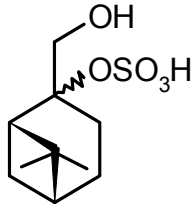
Organosulfates related to  $\alpha$ -pinene detected in ambient fine aerosol include sulfate esters of 2- and 3-hydroxyglutaric acid, hydroxypinonic acid, and isomeric MW 295 nitrooxy organosulfates with a pinane diol skeleton.<sup>336d</sup> Monitoring of the latter nitrooxy organosulfates in field studies revealed that they are nighttime products,<sup>342b,438</sup> pointing to NO<sub>3</sub> radical chemistry. Furthermore, they have also been detected at substantial concentrations in wintertime ambient fine aerosol that is impacted by biomass burning.<sup>444</sup>

The  $\alpha$ -pinene markers discussed above have been analyzed with LC/MS, mainly with ESI or APCI in the negative ion mode, using regular C<sub>8</sub><sup>342b</sup> or C<sub>18</sub><sup>338b,342b,445</sup> and trifunctionally bonded C<sub>18</sub> reversed-phase columns.<sup>40,205,440-441</sup> Some markers such as terpenylic acid can be readily detected in the positive ion mode,<sup>440</sup> while pinic acid, pinonic acid, hydroxypinonic acid and MBTCA can also be analyzed with GC/MS with prior trimethylsilylation.<sup>36,246</sup> However, valuable markers such as the lactone-containing terpenoic acids escape GC/MS detection and may undergo degradation during the derivatization procedure.<sup>441</sup> Therefore, LC/(-)ESI-MS is the technique of choice as it allows to determine established markers such as pinic acid, pinonic acid and hydroxypinonic acid, the novel markers, MBTCA, diaterpenylic acid acetate and the lactone-containing terpenoic acids, as well as  $\alpha$ -pinene-related organosulfates. Quantification of terpenoic acids has been achieved using GC/MS with prior derivatization,<sup>201,446</sup> and more recently with LC/MS based methods.<sup>47,338d,377,445</sup> As for the quantification of isoprene SOA markers, also most methods have not been validated or only partially, again due to the lack of sufficiently pure reference standards or the complete lack of them. Despite these shortcomings, the methods have found to be adequate for determining diel variations and time trends of SOA markers in field monitoring studies.

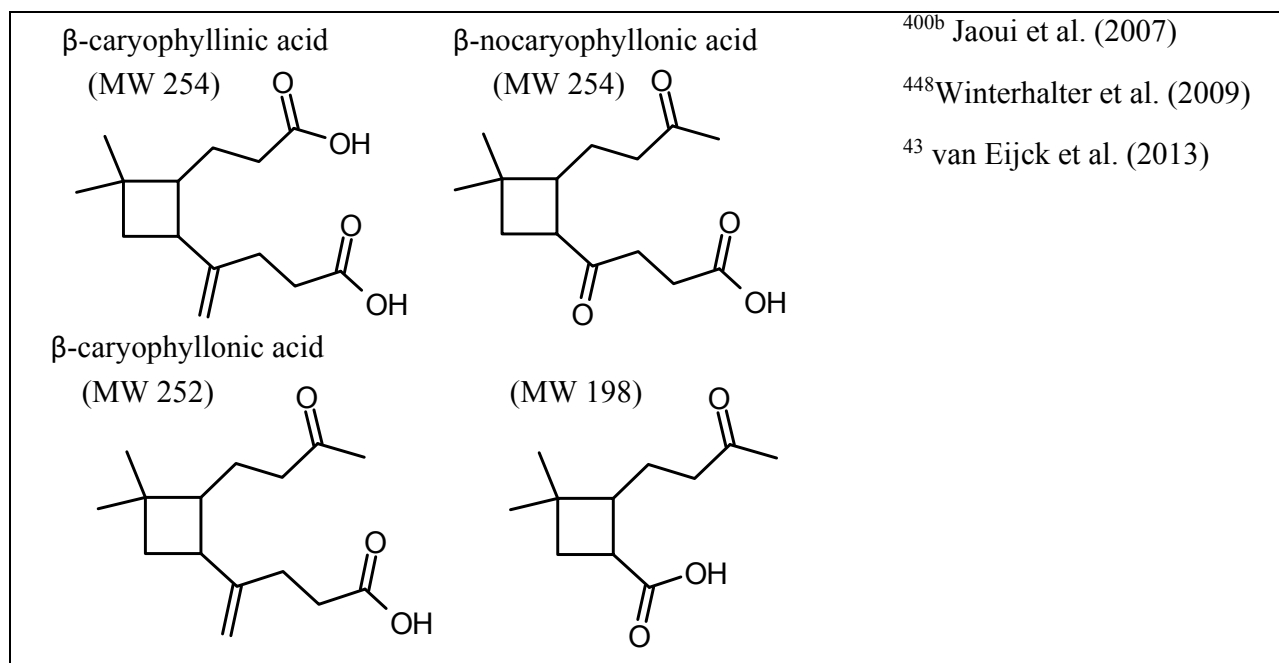
**Other biogenic SOA markers.** Table 9 provides a list of markers which are related to biogenic SOA other than isoprene and  $\alpha$ -pinene SOA and are due to minor monoterpenes (i.e.,  $\beta$ -pinene, *d*-limonene and  $\Delta^3$ -carene) and  $\beta$ -caryophyllene, a sesquiterpene,<sup>43,205,246,338a,400b,447</sup> and have been detected in ambient fine aerosol at substantial concentrations ( $>10 \text{ pg m}^{-3}$ ).<sup>43,338d,445</sup> With regard to  $\beta$ -pinene, it is worth noting that several markers for  $\alpha$ -pinene SOA are also markers for  $\beta$ -pinene, i.e., pinic acid, pinonic acid, terpenylic acid and terebic acid, whereas homoterpenylic acid, a lactone-containing terpenoic acid, is a unique marker which has recently been reported.<sup>205</sup> For the

analysis of the markers listed in Table 9, the same methodology as discussed above for  $\alpha$ -pinene SOA markers can be applied.

**Table 9.** Overview of SOA markers related to  $\beta$ -pinene,  $\Delta^3$ -carene, *d*-limonene and  $\beta$ -caryophyllene, useful for molecular speciation of ambient fine aerosol, and selected references on their structural characterization. Abbreviation: sulfate ester, SE.

Chemical structure and name (MW)		Selected references
<i>Markers for <math>\beta</math>-pinene</i>		
<p><i>cis</i>-pinonic acid (MW 184)</p> 	<p><i>cis</i>-pinic acid (MW 186)</p> 	<p><sup>246</sup> Yu et al. (1999)  <sup>165</sup> Glasius et al. (2000)  <sup>338a</sup> Larsen et al. (2001)  <sup>205</sup> Yasmeen et al. (2011)  <sup>342b</sup> Iinuma et al (2007)</p>
<p>terpenylic acid (MW 172)</p> 	<p>terebic acid (MW 158)</p> 	
<p>10-hydroxy-<i>cis</i>-pinonic acid (MW 200)</p> 	<p>homoterpenylic acid (MW 186)</p> 	
<p>1,2-dihydroxypinane SE (MW 250)</p> 		

<i>Markers for <math>\Delta^3</math>-carene</i>		
<i>cis</i> -3-caronic acid (MW 184)	<i>cis</i> -3-caric acid (MW 186)	<sup>165</sup> Glasius et al. (2000) <sup>338a</sup> Larsen et al. (2001) <sup>205</sup> Yasmeen et al. (2011)
10-hydroxy- <i>cis</i> -3-caronic acid (MW 200)	terebic acid (MW 158) (see above)	
<i>Markers for d-limonene</i>		
ketolimononic acid (MW 186)	limonic acid (MW 186)	<sup>165</sup> Glasius et al. (2000) <sup>338a</sup> Larsen et al. (2001) <sup>447</sup> Jaoui et al. (2006) <sup>336d</sup> Surratt et al. (2008) <sup>205</sup> Yasmeen et al. (2011)
ketolimononic acid (MW 188)	3-carboxyheptanoic acid (MW 204)	
1,2-dihydroxy-4-acetylcyclohexane nitrooxy organosulfates (MW 298)		
+ positional isomer		
<i>Markers for <math>\beta</math>-caryophyllene</i>		



#### 5.1.4. Future directions in the investigation of SOA

As emphasized in this chapter, the identification, quantification and other characterization of atmospheric SOA involve many challenges. Many of the difficulties and controversies in characterizing atmospheric SOA result from their unspecific and process-based definition. It is thus time for the atmospheric community to propose (a) more specific definition(s), better adapted to the current understanding of these aerosols and to current instrumental capacities, for instance making a distinction between the SOA obtained from condensation and those obtained from surface- or condensed-phase reactions. Important progress has however been achieved over the past three decades, where organic identification has played a key role. The SOA originating from major (isoprene and  $\alpha$ -pinene) and other BVOCs (e.g.,  $\beta$ -pinene,  $\Delta^3$ -carene, *d*-limonene, and  $\beta$ -caryophyllene) is now well characterized at the molecular level and suitable markers for source apportionment and field monitoring are available. But the SOA produced by oxygenated BVOCs, such as the C<sub>6</sub> green leaf volatiles, emitted by wounded or insect-infested plants, is largely



unexplored in spite of the evidence that they are a source for SOA.<sup>338d,449</sup> Methods for the quantitative determination of SOA markers using GC/MS with prior derivatization or LC/MS are still only partially validated and could benefit from interlaboratory comparisons. In addition, laboratories involved in molecular speciation would welcome the availability of mass spectral libraries so that SOA markers could more readily be identified, without requiring authentic standards.

In addition, a new direction of research in this topic, which has developed over the last decade, is the investigation of the condensed-phase reactions contributing to SOA mass, composition, and properties. An important future direction of investigation in this topic appears to be the reactions in neutral ammonium seeds. Other important directions of research in the near future will be the characterization of important SOA properties such as their O/C and H/C ratios, optical properties (Chapter 5.3), and cloud-forming properties (Chapter 5.4). Organic identification will continue to be key in exploring all these questions.

## **5.2. Biomass burning aerosols**

### **5.2.1. Background**

Biomass burning aerosols originate both from anthropogenic and natural combustion such as wild fires, agricultural fires, deforestation fires, and residential biomass combustion for cooking and heating. Carbonaceous aerosols from biomass burning are of scientific and public interest because of their occurrence in local, regional and global environments as well as their impact on human health, air quality, visibility, and climate. Globally, biomass burning is one of the major sources of primary organic aerosols, light-absorbing carbon (brown and black carbon, see Chapter 5.3),<sup>450</sup> and probably also of SOA.<sup>451</sup> It has been shown to have adverse health effects such as respiratory diseases.<sup>452</sup> In low- and middle-income countries the indoor combustion of solid fuels

(including biomass) is estimated to cause about 2 million deaths annually.<sup>452b</sup> Even in high-income countries biomass burning for residential heating has detrimental effects on human health,<sup>452a,453</sup> although further investigations are warranted to constrain its local and regional impact. Biomass burning aerosols can contribute to the climate budget directly, i.e., through its light-absorbing carbon component (Chapter 5.3), but also indirectly by affecting the formation or optical properties of clouds (Chapter 5.6).<sup>450a</sup>

The main challenges concerning biomass burning are to determine its sources and impacts on regional and local air quality. This is achieved by “source apportionment” approaches, which are based on the identification and quantification of specific molecular markers, such as anhydromonosaccharides (levoglucosan, mannosan, and galactosan) formed by the pyrolysis of cellulose and hemicelluloses.<sup>454</sup> But large uncertainties remain in these determinations, requiring more studies, in particular the identification of additional markers. The information about the impact of biomass burning on ambient air quality is especially important for a regulatory body to decide if biomass burning should be regulated or controlled. The characterization of markers in such varied and complex mixtures of organic compounds, including non-polar hydrocarbons to very polar saccharidic compounds, is a showcase for the capability of analytical methods towards molecular identification.

### **5.2.2. Molecular organic markers**

The chemical composition of the biomass and type of combustion sustained directly influence the physical and chemical properties of the resulting biomass burning aerosols. Different tree species develop markedly different woody constituents during growth, but all wood consists of various forms of lignin, cellulose and fillers.<sup>455</sup> At temperature below 300 °C reduction of MW, evolution of water, CO<sub>2</sub> and CO is observed. While at temperatures between 300 – 500 °C the

biopolymers rapidly undergo bond cleavage yielding monomeric compounds, at higher temperatures, wood molecules dehydrate, disproportionate and decarboxylate giving rise to low-MW products.<sup>456</sup> In the following section, we separate biomass burning marker compounds into non-polar, polar and SOA compounds based on suitable analytical techniques for each compound group. As biomass burning aerosols contain a large number of organic compounds with a wide range of properties, it is important to choose a suitable analytical method for the accurate quantification of the marker compounds.

#### **a) Non-polar marker compounds**

Non-polar marker compounds in biomass burning smoke have been almost exclusively analyzed using GC/MS based methods. These marker compounds are a wide array of low-MW organic compounds, which originate from extractives in biomass and constitute 4-10% dry mass of normal temperate wood species.<sup>455</sup> The extractives contain fats and waxes, terpenoids, resins, essential oils, mono- and disaccharides, and monomeric phenolic compounds.<sup>457</sup> They serve as metabolic intermediates, defense chemicals against predators, or energy reserves. During wood combustion, the extractives and their thermal degradation products are released by volatilization and steam distillation. Some of the organic constituents in the extractives are unique to certain wood types and can be used as marker compounds for source identification of atmospheric aerosols.<sup>458</sup>

A group of non-polar compounds present at elevated concentrations in wood-smoke emissions (but not specific to wood combustion) are *n*-alkanes, *n*-alkenes, *n*-alkanols and *n*-alkanoic acids that originate from epicuticular waxes and lipids. *n*-Alkanes emitted from biomass burning show a distinctive odd to even carbon predominance (carbon preference index >1), especially for higher carbon number homologues with a  $C_{max}$  value between  $C_{25}$  and  $C_{31}$ .<sup>458b,459</sup> On the other hand, *n*-alkenes, *n*-alkanols and *n*-alkanoic acids show predominantly even carbon preferences (carbon

preference index  $<1$ ).<sup>459b-459d,460</sup> *n*-Alkanoic acids react with ammonia in biomass combustion processes, forming alkyl amides and alkyl nitriles<sup>461</sup> though little is known about the formation mechanisms and concentrations of the latter derivatives in wood smoke. While biomass burning markers originating from plant waxes and their alteration products are not source specific, they are typically found in particles smaller than  $1\ \mu\text{m}$ <sup>459b</sup> whereas biologically emitted plant waxes are found mostly in particles larger than  $1\ \mu\text{m}$ .<sup>462</sup> Hence, the difference in their size distribution can be used as a fingerprint for the influence of wood smoke in ambient aerosols. *n*-Alkanes, *n*-alkenes, alkyl amides and alkyl nitriles can be analyzed with GC/MS without prior derivatization steps. *n*-Alkanols and *n*-alkanoic acids are typically analyzed using GC/MS based methods with a prior derivatization step, either the alkylation of carboxylic OH groups or the trimethylsilylation of all hydroxyl groups.<sup>458b</sup>

Although polycyclic aromatic hydrocarbons are not unique marker compounds for wood combustion, their occurrence in wood smoke has been known for a long time<sup>463</sup> and their identification and quantification in wood smoke has been considered important because of their potential impact on public health. Various analytical techniques have been applied to determine PAHs in ambient aerosol samples in the past though GC/MS based methods have been most widely used due to their good chromatographic separation and detector sensitivity. Their application to the analysis of PAHs in atmospheric samples has been reviewed very recently.<sup>464</sup> Among PAHs detected in wood smoke, retene is considered to be a unique marker compound for coniferous wood combustion. This compound is suggested to form from thermal degradation of resins, most likely diterpenoids such as abietic acid in the conifer resins.<sup>465</sup>

Sample preparation procedures for the analysis of non-polar biomass burning markers with GC/MS typically involve organic solvent extraction, clean up and pre-concentration steps prior to

analysis. Alternatively, thermally assisted desorption systems such as a Curie-point pyrolyzer<sup>459b,466</sup> and a variation of self-made or commercially available thermal desorbers<sup>258-259,467</sup> may be used to inject collected aerosol samples directly into GC/MS systems. In comparison to a number of studies reporting their emission factors from combustion sources and concentrations in atmospheric samples, little is reported about artifact formation during sample work-up procedures. Owing to the extremely complex nature of biomass burning samples, the determination of recovery values for all the compounds detected may be unrealistic. Nevertheless, reliable quantification of these marker compounds may still be possible when isotope-labeled authentic standard compounds are used as internal standards.

#### **b) Polar marker compounds**

There are several methods available to analyze polar marker compounds in biomass burning smoke. Traditionally, GC/MS with a prior derivatization step has been used for the characterization of polar marker compounds. Liquid-based separation techniques coupled to mass spectrometry have become more popular tools in recent years due to their simpler sample preparation procedures for the analysis of polar compounds.

Among polar marker compounds, the pyrolysis products of cellulose and hemicelluloses are the most important class of compounds in biomass burning smoke. Cellulose is a macromolecule consisting of several to ten thousand linearly linked D-glucopyranose units, whereas hemicelluloses are smaller macromolecules that contain different monosaccharidic (e.g., mannose and galactose residues) but mainly D-glucopyranose units. Cellulose and hemicelluloses provide a supporting mesh for wood structures and account for 30-40% of woody tissue.<sup>456</sup> The major pyrolysis products of cellulose and hemicelluloses are anhydromonosaccharides, namely levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose), galactosan (1,6-anhydro- $\beta$ -D-galactopyranose)

and mannosan (1,6-anhydro- $\beta$ -D-mannopyranose), and they are widely used as biomass burning marker compounds because they are specific and emitted in considerable amounts.<sup>454</sup>

Another class of polar biomass burning marker compounds is the pyrolysis products of lignin. Lignin is an amorphous biopolymer synthesized by monolignols and accounts for 25-35% of the dry mass of softwood and 18-25% of hardwoods. Its function is to provide strength and rigidity to plant structures.<sup>456,468</sup> Its pyrolysis produces mostly substituted phenols and substituted methoxyphenols with predominantly *p*-coumaryl alcohol derivatives from grass combustion, *p*-coniferyl alcohol derivatives from softwood combustion and sinapyl alcohol derivatives from hardwood combustion. This difference may be used as an indicator for the influence of soft- or hardwood combustion in ambient aerosols.<sup>469</sup>

Among the extractives, resins and their thermal degradation products such as abietic acid, dehydroabietic acid and oxo-dehydroabietic acids are often present in wood smoke influenced ambient aerosols.<sup>458b,458c</sup> These compounds are specific to the combustion of temperate coniferous trees, and can be considered as marker compounds for their combustion.

Owing to the presence of polar functional groups in their structures, resin-related markers are best analyzed with GC/MS methods with prior derivatization such as trimethylsilylation.<sup>230,258,454c,458a,460,470</sup> Alternatively, substituted phenols, substituted methoxyphenols and abietic acid derivatives can be analyzed underivatized with liquid-based separation techniques coupled to mass spectrometry such as CE/MS<sup>459b</sup> and LC/MS.<sup>444,471</sup> In addition, anhydromonosaccharides can be analyzed with HPAEC coupled to a pulsed amperometric detector (PAD),<sup>286,472</sup> HPAEC coupled to a mass spectrometric detector,<sup>291,298</sup> microchip CE coupled to a PAD<sup>473</sup> and HPLC/ESI-MS.<sup>474</sup> The liquid-based separation techniques have advantages over traditional GC/MS analysis with a prior derivatization step in that their

sample preparation procedure is simpler and they enable the direct analysis of aqueous samples such as fog or cloud samples.<sup>475</sup>

Extraction and derivatization steps for GC/MS methods have been extensively characterized and optimized for anhydromonosaccharides<sup>230,470d,476</sup> and methoxyphenols.<sup>477</sup> For example, the evaporative loss of methoxyphenols during Teflon filter extraction with a mixture of methylene chloride/acetone under ultrasonication was found to be a significant problem,<sup>477</sup> and they an extraction with ethyl acetate in a sealed headspace vial was chosen, which yielded a median recovery value of 97% for deuterium-labeled recovery standard compounds. For anhydromonosaccharides, the extraction recovery of levoglucosan was optimized using a dichloromethane/methanol mixture (80:20, v/v), yielding  $90.0 \pm 2.4 - 97.0 \pm 4.0\%$ .<sup>446</sup> A 99% recovery of anhydromonosaccharides was reported after two consecutive extraction steps from spiked quartz fiber filters with tetrahydrofuran as an extraction solvent for an HPLC/MS method.<sup>474a</sup> A recovery of  $95 \pm 3\%$  was reported for levoglucosan from spiked quartz fiber filters by two consecutive water extraction steps with short vortex agitation and gentle shaking.<sup>478</sup> A nearly complete extraction of monoanhydrosaccharides from quartz fiber filters was also reported with water by ultrasonic agitation,<sup>286,472e</sup> and by short vortex agitation and gentle shaking.<sup>298</sup>

### **c) Biomass burning SOA marker compounds**

Until recently, little was known about the formation of SOA in biomass burning and its marker compounds. The formation of SOA in biomass burning smoke was suggested from the aqueous phase-reactions of lignin products such as phenol, guaiacol and syringol in laboratory experiments.<sup>479</sup> In these studies, HPLC-UV was used to follow the decay of the precursor compounds and the product formation was assessed by HR-AMS. Similarly, the photochemical oxidation of wood smoke and changes in its chemical characters was investigated in a smog

chamber.<sup>451,480</sup> In these studies, changes in AMS mass fragments were used to identify the oxidation of primary aerosols and the formation of biomass burning SOA. Another chamber study investigated the formation of SOA from the gas-phase photooxidation of biomass burning marker compounds such as phenols and methoxy-phenols.<sup>481</sup> In this study, the gas-phase oxidation products were detected using CI-MS with  $\text{H}_3\text{O}^+$  as a reagent in the positive mode and  $\text{CF}_3\text{O}^-$  as a reagent in the negative mode, whereas UPLC/ESI-MS was used for the analysis of SOA compounds. Based on the results from these experiments, the authors cautioned that the use of guaiacol (softwood combustion marker) and syringol (hardwood combustion marker) may not be a suitable marker for atmospheric aerosol as syringol can efficiently form guaiacol and other hydroxylated aromatic compounds during the photooxidation.

Series of smog chamber experiments indicate that the oxidation in the presence of  $\text{NO}_x$  of *m*-cresol, which is largely emitted from wood combustion,<sup>482</sup> forms methyl-nitrocatechols.<sup>483</sup> In atmospheric aerosols nitro-aromatic compounds have been reported to correlate very well with levoglucosan in wintertime and thus suggested to be suitable molecular markers for biomass burning SOA.<sup>444,483</sup> They were also found in the HULIS fraction of biomass burning-influenced aerosols from Hungary and Brazil.<sup>333</sup> In all these studies the identification of the nitro-aromatic compounds was achieved by comparing the LC retention times and MS fragmentation patterns of the compounds present in the atmospheric samples, those present in laboratory-generated aerosols, and authentic standards. Very recently, the HPLC/ESI-MS/MS analysis of a series of nitro-aromatic compounds in ambient aerosols was improved<sup>379,387</sup> by separating isobaric isomers, notably of methyl-nitrocatechols and nitro-guaiacol, by substituting acetonitrile with tetrahydrofuran in the LC eluent. The latter method also uses ethylenediaminetetraacetic acid to



resolve the peak shape distortions of some of nitro-aromatic compounds forming transition metal complexes.

### **5.2.3 Future directions in the investigation of biomass burning aerosols**

Over the past two decades significant progress has been made in the identification and quantification of organic markers of biomass burning aerosols. But despite the large body of data obtained little effort has been done to compare or standardize the different analytical procedures. In particular, as the determination of the concentrations of anhydromonosaccharides in ambient aerosols is becoming a routine analysis, reliable analytical procedures are urgently desirable. In order to address this need an interlaboratory comparison for the determination of levoglucosan, mannosan and galactosan in ambient filter samples has recently been organized (Chapter 3.3).<sup>37</sup>

Another area of uncertainties is the further oxidation of particle-bound biomass burning markers and their products in the atmosphere, which limits the accuracy in the contribution of biomass burning determined in source apportionment studies. Atmospheric stability has been only investigated for levoglucosan, the most abundant biomass burning marker.<sup>454b</sup> But the results of solar radiation experiments, and acid hydrolysis experiments<sup>470a,484</sup> showing the stability of this compound have been recently contradicted by aqueous-phase<sup>485</sup> and gas-phase<sup>486</sup> oxidation experiments with OH radicals concluding in a half-life of 3 to 4 days in wintertime deliquescence particles<sup>485</sup> and of 0.7 to 2.2 days in the gas phase in summertime.<sup>486</sup> Further studies of the oxidation of other biomass burning markers and their products are therefore warranted to improve the source apportionment of biomass burning.

In general, further laboratory, field and remote-sensing studies are needed to constrain the emission factors, and spatial and temporal distributions of biomass burning marker compounds, SOA formation, and relevant physico-chemical properties to obtain better estimates of the global

and regional biomass burning emissions and of its contributions to air quality, public health, and climate.

### **5.3. Optically-active compounds**

This chapter focuses on another important class of organic compounds in the atmosphere: those displaying specific properties upon interaction with solar light. Solar radiation is the main source of energy in the Earth's atmosphere and atmospheric components can interact with it in two ways: by absorbing or scattering it. This can give them different roles: a contribution to the Earth's radiative budget (either a warming or a cooling one), or a role as photochemical precursor in atmospheric chemistry. In particular, obtaining an accurate radiative budget depends on the ability to fully inventory all the absorbing or scattering components present in the atmosphere. Identifying the organic compounds or classes of compounds taking part in these processes is therefore important. This chapter summarizes the current knowledge of these compounds, their roles in the atmosphere, and discusses potential future areas of investigations.

#### **5.3.1. Organic compounds contributing to the direct radiative forcing**

Both organic gases and particulate matter present in the atmosphere absorb and scatter light. Scattering by atmospheric gases (Rayleigh scattering) is generally not taken into account in atmospheric chemistry or the climate budget because it reflects light in all directions and does not affect the radiative balance. Thus only organic gases absorbing light are discussed below. Atmospheric particles can either absorb solar energy and contribute to warm climate, or scatter it back to space (Mie scattering) and contribute to cool it. Until recently organic aerosols were assumed to be mostly scattering (see discussion below), therefore this sub-chapter will focus on the more recent evidences for their light-absorbing properties (brown carbon).

##### **a) Greenhouse gases**

As explained in Section 4.1.1, all organic compounds absorb light in the IR region (wavelength,  $\lambda > 800$  nm), where the energy is transferred into rotational and vibrational molecular motions and ultimately heat. Most of them also absorb in the near UV and Visible region ( $\lambda < 800$  nm) and transform some of the energy into heat, either directly or by recycling photochemical energy. Thus, all their absorbing properties can potentially contribute to warm the radiative budget. However, only the gases absorbing at different wavelengths than important atmospheric constituents, in particular water vapor, effectively have a warming contribution and are called greenhouse gases (GHG). Organic GHGs include methane ( $\text{CH}_4$ ), chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), and hydrochlorofluorocarbons (HCFCs).<sup>487</sup> Their presence and abundance in the atmosphere is mostly inferred from chromatographic analyses (GC-FID or GC/MS) such as described in Chapter 4.2.2. In spite of the large number of atmospheric CFCs and HCFCs already known several new ones have recently been identified by GC/MS.<sup>488</sup> Thus, it cannot be excluded that more remain to be identified.

The contributions of the organic GHGs other than  $\text{CH}_4$  to the global radiative budget are however modest.<sup>487b</sup> All together, they represent less than  $0.5 \text{ W m}^{-2}$ , while  $\text{CH}_4$  alone contributes for the same amount and  $\text{CO}_2$  for about  $1.8 \text{ W m}^{-2}$ . The individual contributions represent only a few % of the total GHG forcing (in  $\text{W m}^{-2}$ ): CFC-11, 0.06; CFC-12, 0.17; HCFC-22, 0.04; others,  $< 0.03$ . The contribution of yet unknown organic GHGs is thus likely to be small, especially because the probability that their IR spectrum does not overlap with those of previously known GHGs is getting smaller with each new compound. Thus the identification of new organic GHGs should not significantly improve the global radiative budget. Note, however, that beside GHGs, nearly all organic gases contribute to the global radiative forcing by producing  $\text{O}_3$ , another important GHG, as a side-product of their oxidation in the presence of  $\text{NO}_x$ . But since these processes are not

directly related to their optical properties they are not discussed here. Some studies have estimated the radiative contribution of all organic gases at regional or local scale, but mostly in the UV-Vis region: nitrated aromatic gases were thus estimated to about  $1 \text{ W m}^{-2}$  in the UV range in the Los Angeles basin, and total organic gases (29 compounds including carbonyls, organonitrates, peroxides, and phenols) to about twice as much.<sup>489</sup> Identifying and inventorying the light-absorbing organic gases in some regions can thus be important when estimating the visibility and radiative balance.

#### **b) Brown carbon**

For decades “black carbon”, also termed “elemental carbon” or “light-absorbing carbon”, was the only carbonaceous material thought to absorb in this spectral region. The assumption that organic material does not absorb light is still largely made today, especially in climate models (see discussion below). However, evidence of the contrary has been accumulating for decades, facilitated by the clear contrast between the strong wavelength dependence of the spectrum of organic compounds and the nearly-constant spectrum of black carbon.<sup>490</sup> A strongly wavelength-dependent spectrum, revealing the presence of absorbing organic material, was reported for organically-extracted fractions of ambient aerosols as early as the 80’s.<sup>491</sup> This material was compared to humic substances and given the name of “brown carbon”. Organic fractions with similar wavelength-dependent spectra were subsequently identified from coal burning,<sup>492</sup> biomass burning,<sup>493</sup> and urban/road-side aerosols.<sup>494</sup> This evidence, obtained by chemical analyses, was confirmed by very different approaches such as ground-based measurements of aerosol light-attenuation,<sup>495</sup> irradiance,<sup>496</sup> or sun photometer measurements, in particular with the AERONET network.<sup>497</sup> The latter evidenced not only similar wavelength dependences in the absorbance of ambient aerosols but clearly demonstrated that brown carbon affects their overall optical

properties. Brown carbon seems therefore to be an important component to take into account when estimating the optical and radiative properties of aerosols. Taking into account brown carbon in the overall aerosol absorbance has also been underlined as essential in order to correctly attribute the contributions of black and elemental carbon, the errors made otherwise being estimated to a factor 2 to 7.<sup>490</sup> An emerging challenge in the determination of global or regional radiative budgets is therefore the identification of all the types and sources of brown carbon. So far, the following types have been reported:

- **Combustion and biomass burning brown carbon:** the reader is referred to Chapter 5.2 for details on the organic composition of biomass burning aerosols. Generally, their “optically-active” components have been identified as polyaromatic material such as PAHs and oxygenated PAHs,<sup>490</sup> and nitro-aromatic compounds.<sup>276</sup>

- **HULIS.** Some atmospheric aerosols have been found to contain light-absorbing macromolecular fractions having properties similar to those of humic substances, and therefore termed humic-like substances.<sup>333,354,491,498</sup> However, the definition of atmospheric HULIS being based on their extraction procedure,<sup>491,498a,498b</sup> it is difficult to attribute them to a single compound or source. HULIS are often linked to biomass burning aerosols<sup>491</sup> but have also been found in a wide range of atmospheric aerosols, including rural and remote ones.<sup>333,498a,498b</sup> Their smaller molecular mass (<400 Da) than terrestrial humic substances questions their similarities with the latter, and their sources have been suggested to be secondary rather than primary.<sup>498d</sup> The analyses of HULIS report a complex chemical composition, which has remained an identification challenge for years. Increasingly sophisticated techniques, including electrospray ionization in combination with tandem and high-resolution mass spectrometry<sup>333,354,498c,498e</sup> have been used to investigate their molecular structures and sources. They identified aromatic compounds, polysaccharides, and

aliphatic compounds with polar groups such as hydroxyl, carboxy, carbonyl, nitrate and sulfate among the components. More recent studies<sup>333</sup> confirmed the small MW range of atmospheric HULIS (<300 Da) and identified nitro-catechols as the main chromophores in urban and tropical biomass burning HULIS, while organic tri-acids and terpenic acids dominated rural ones. These results confirm the multiplicity of types and sources of atmospheric HULIS, and the challenge involved in determining their contributions to brown carbon.

- **biogenic primary organic matter and POA:** Although the presence of biological material (plant debris, cellular debris, pollen, bacteria, etc) in the atmosphere is known for a long time,<sup>499</sup> it has mostly been discussed as an aerosol type (Primary Biological Atmospheric Particle, or PBAP) and much less at the molecular level. The biological molecules identified so far in aerosols include amino acids, proteins, sugars, polysaccharides, and fatty acids, which do not absorb in the UV-Vis region. However some PBAPs have been shown to absorb sunlight and most of them are considered to be fluorescent (see below). The molecules responsible for the absorption have not been identified but could be related to strong biological UV-Vis absorbers such as chlorophylls, carotenoids, and tannins. But the molecular structure and impact on the aerosol properties of this “biological brown carbon” remain largely to be investigated.

- **Secondary organic material.** As discussed in the previous chapter, a number of condensed-phase reactions in SOA produce light-absorbing compounds, such as aldol condensation producing C=C conjugated compounds<sup>414b,416c,416g,419,420b,420c,500</sup> and the condensation of dicarbonyl (glyoxal, methylglyoxal) or larger carbonyl compounds with  $\text{NH}_4^+/\text{NH}_3$ <sup>72a,80,414b,423,424d,425</sup> or with trace compounds such as amino acids and amines,<sup>424</sup> all producing conjugated C-N compounds such as imidazoles. While all these products display a main absorption band below 350 nm, a condensation product of limonene keto-aldehyde with  $\text{NH}_4^+/\text{NH}_3$  was recently reported to have a maximum

absorbance near 500 nm, thus fully in the visible range.<sup>80,424d,425</sup> The molecular identification of such highly conjugated compounds is a challenge because they have intense absorption coefficient, but are produced in trace concentrations in complex product mixtures. Nonetheless, structures were proposed for this and other compounds obtained under similar conditions from other SOA precursors, based on extraction and ESI-HR-MS analyses.<sup>501</sup> A main challenge in this field of research is now to identify such secondary brown carbon in ambient aerosols using similar types of analyses, identify and quantify their formation mechanisms, and accurately determine their impacts on the optical and radiative properties of organic aerosols.

The contribution of brown carbon to the global radiative budget is currently not well taken into account in climate models. All of the 14 climate models taken into account in the latest IPCC report included primary organic carbon, and the implementation of SOA in about half of them (8 out of 14) was underlined as an important improvement compared to previous IPCC reports.<sup>502</sup> However, this effort was exclusively made on the modeling of the SOA microphysics (formation rates, mass loadings, size distribution), while their absorption indices, along with those of POA, were still based on non peer-reviewed and pre-2000's estimates<sup>503</sup> or sub-module calculations<sup>504</sup> assuming a negligible absorption index for organic matter at all wavelengths. One exception is the HITRAN database,<sup>505</sup> which includes more realistic optical properties for brown carbon. However, the proxy chosen for SOA are laboratory reactions with amines,<sup>424c</sup> which are less representative of aerosol brown carbon than the products obtained with  $\text{NH}_4^+/\text{NH}_3$ , but can be easily updated with the references cited in this review. Therefore, adding SOA to the climate models in the 2013 IPCC exercise while still neglecting their absorbance merely introduced an additional scattering component in the radiative budget and resulted in a seemingly larger cooling contribution of aerosols than in previous reports.

A number of observations, however, support a significant warming contribution of brown carbon to the global aerosol forcing, such as the multi-wavelength ground-based measurements of aerosol radiation showing a brown carbon contribution of 28% of the total light absorption at 440 nm in California.<sup>497a</sup> applying the same method at global scale estimated the global contribution of brown carbon between 0.1 and 0.25 Wm<sup>-2</sup> and changed the global contribution of aerosols from the current cooling one to a warming one (+ 0.025 W m<sup>-2</sup>).<sup>497b</sup> These results underline the substantial errors made in current climate models by neglecting the absorbance of brown carbon, and the urgency to better characterize the optical properties of the different types of brown carbon.

### 5.3.2. Light-absorbing compounds as photochemical precursors

#### a) Gases

The absorption of sunlight by organic compounds in the UV or Vis region triggers electronic transitions, and confers to organic compounds photochemical properties. These transitions often correspond to bond-altering processes such as photolysis or energy exchanges such as photosensitization or fluorescence, and often result in the formation of free radicals. Most of the organic gases absorbing in the UV-Vis region (thus at  $\lambda \geq 290$  nm) in the atmosphere photolyze and produce radicals. Table 10 summarizes the main types of gases having these properties: aldehydes, dicarbonyls, ketones, peroxides, organo-nitrates, and some aromatic compounds such as nitro-phenols. Their importance as radical precursors depends on the product of their absorption cross section by their quantum yield, which are compared for the ground-level cut-off wavelength of 290 nm in Table 10.<sup>506</sup>

**Table 10.** UV-Vis absorbing organic gases in the atmosphere, with the position of their absorption band, absorption cross sections,  $\sigma$ , and photolysis quantum yield,  $\Phi$ , at 290 nm.

Gas	$\lambda_{\text{max}}$ (nm)	$\sigma(290 \text{ nm}) \times 10^{20} \text{ molec cm}^{-2}$	$\Phi(290 \text{ nm})$	Ref
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HCHO	~ 305	1.2	1.0	506a
CH <sub>3</sub> CHO	290	4.9	0.5	506a
CHOCHO	298	3.9	0.6	506a
CH <sub>3</sub> (CO)CH <sub>3</sub>	274	4.9	0.4	506a
CH <sub>3</sub> OOH	< 210	0.7	1.0	506a
CH <sub>3</sub> (CO)OH	205	< 0.1		506b
CH <sub>3</sub> OH	184	< 0.01		506b
CH <sub>3</sub> ONO <sub>2</sub>	190	0.9	1.0	506a
CH <sub>3</sub> O <sub>2</sub> NO <sub>2</sub>	< 200	3.9	1.0	506a
CH <sub>3</sub> (CO)ONO <sub>2</sub>	< 200	0.5	1.0	506a
Nitro-phenols	320 - 360	?	?	506d
Naphtalene				
Anthracene	312 - 365			

The importance of organic gases as sources for radicals, such as OH and HO<sub>2</sub> (HO<sub>x</sub>), or other important compounds for atmospheric chemistry such as NO<sub>x</sub> or HONO, depends not only on their spectroscopic properties (Table 10) but also on their atmospheric concentrations. Thus, while the photolysis of organic gases is estimated to be globally a minor source of HO<sub>x</sub> radicals in the atmosphere, formaldehyde (HCHO) is estimated to be the main organic contributor to HO<sub>x</sub> because of its abundance. In some regions, however, the contribution of photolyzable organic gases to the radical budget can be much more important. In a tropical rainforest, the photolysis of organic hydroperoxides (CH<sub>3</sub>OOH, ROOH) has a small but non negligible contribution to the HO<sub>x</sub> budget.<sup>507</sup> At a rural and forested site the photolysis of HCHO and other organic compounds was estimated to contribute to 23% of the radical sources.<sup>508</sup> And in an urban environment such as Mexico City the photolysis of HCHO alone was estimated to contribute to 69% of the direct HO<sub>x</sub>

sources, and dicarbonyl compounds (glyoxal, methylglyoxal) and other aldehydes to an additional 17% (Figure 9). The photolysis of other organic compounds also contributed indirectly to the HO<sub>x</sub> sources by producing organic radicals.<sup>509</sup> In a previous campaign at the same location these contributions were estimated to be even larger, the HO<sub>x</sub> sources being almost entirely accounted for by the photolysis of HCHO (over 50%) and other oxygenated compounds (glyoxal, acetaldehyde, ketones..., about 45% in total).<sup>510</sup> The importance of optically-active organic gases in atmospheric chemistry is therefore not questionable. The contribution of photolyzable organic gases to the radical sources in the atmosphere is currently thought to be well understood. However the current unknowns in the radical cycles today (Chapter 5.6) do not entirely preclude the existence of yet unknown organic gas-phase sources for radicals.

#### **b) Particulate matter**

As in the gas phase, some organic compounds present in or at the surface of aerosols or cloud droplets can photolyze when exposed to UV-Vis light. The depth at which shortwave radiations can penetrate atmospheric particles is however unclear and can limit direct photolysis in the bulk. Photosensitization can provide alternative radical sources to direct photolysis. A photosensitizer is a compound absorbing light, which, instead of photolyzing, transfers its excitation energy to another compound, thus triggering reaction chains that are propagated by charge or electron exchanges (radical reactions) and terminated by electron acceptors. Photosensitized processes of atmospheric relevance have been evidenced at the surface of aerosol proxies in laboratory, such as the photo-induced formation of HONO,<sup>511</sup> uptake of ozone,<sup>512</sup> or heterogeneous ozonolysis reactions.<sup>513</sup> More recently similar processes were also evidenced in the aerosol bulk, and shown to contribute to SOA growth via bulk radical reactions.<sup>428,514</sup> In these studies the organic photosensitizers used were humic acids,<sup>511,514a</sup> benzophenone and benzoic acid-related

compounds,<sup>512-514</sup> and imidazoles.<sup>428,514b</sup> While humic substances and their proxies, benzophenone and benzoic acid, might not be present in all aerosols, the fact that secondary products of simple precursors, such as imidazoles from glyoxal, can also act as a photosensitizer indicates that such processes could be more common in the atmosphere than previously thought, and might be a source for radicals both in the particulate and in the gas phase, which remains to be evaluated.

### **c) Fluorescent organic compounds**

Beside the photolyzable organic compounds discussed above, highly conjugated compounds such as polyaromatic ones containing 2 to 4 rings are also present as gases in the atmosphere. But they do not photolyze<sup>515</sup> in spite of their strong absorption in the near UV and Vis regions, thus do not contribute to the gas-phase radical sources. This is because their molecular structures allow for more complex transitions, such as fluorescence. When present in or at the surface of atmospheric particles such fluorescent properties can be accompanied with photosensitizing abilities,<sup>516</sup> as described above, making of these compounds potential radical sources in the particulate phase.

These compounds can be monitored with fluorescent detectors, which were developed about two decades ago to monitor airborne bacteria and biochemical warfare, but later widely used to investigate atmospheric aerosols for scientific purposes.<sup>517</sup> It is well established, however, that not all biological material fluoresces, and that some non-biological material fluoresces and can interfere with these measurements. Examples of the latter are aromatic compounds and PAHs, which are responsible for the fluorescent properties of cigarette smoke. HULIS are also known to fluoresce<sup>498b</sup> although they are not necessarily biogenic. More recently, laboratory studies have evidenced the fluorescent properties of reaction products of organic compounds with  $\text{NH}_3/\text{NH}_4^+$ .<sup>518</sup> The identification of biological compounds by fluorescence is thus interesting but subject to a

number of limitations and artifacts. On the other hand, fluorescence can be used to identify the conjugated compounds, some of them having interesting photochemical properties.

### **5.3.3. Perspectives on optically-active organic compounds**

As discussed in this chapter, the role of atmospheric organic gases in the radiative budget is fairly well established, as well as their role as sources for radicals or other important species, although the current unknowns in the oxidizing cycles of the atmosphere do not exclude some unexpected contributions of optically-active organic compounds. But, by far and large, most of the current challenges and uncertainties on the optically-active organic compounds in the atmosphere concern the condensed material: the nature and contribution of brown carbon to the radiative budget, and the nature, abundance, and role of photochemical precursors (or photosensitizers) in atmospheric particles. The non-negligible contribution of brown carbon to the optical and radiative properties of ambient aerosols is now supported by a very large number of direct observations. It is thus urgent to finally include realistic absorption indices for brown carbon in climate models, potentially making the global forcing of aerosols positive (warming) instead of negative (cooling). The potential importance of photosensitized processes in or at the surface of particles in the atmosphere just begins to be revealed by laboratory studies, but already justifies further investigations. In both cases, future investigations will have to determine the types of compounds or structures taking part in these processes in the atmosphere and their sources, thus identify their markers in ambient aerosols. Although these compounds are only interesting for their optical properties, the identification of their specific sources will require the molecular identification of specific markers with advanced analytical techniques such as LC/MS, in combination with soft ionization and HRMS. This effort is well underway for HULIS and biomass burning material, but remains almost entirely to be done for light-absorbing components of SOA and POA, and for

potential photosensitizers present in aerosols. Thus, as with most of the topics involving organic compounds, molecular identification will be key in improving the knowledge of these compounds and of their role in the atmosphere.

#### **5.4. Cloud-forming organic material**

Clouds are important components of the atmosphere, not only for their role in the hydrological cycle but also because they are among the main cooling factors in the climate budget.<sup>519</sup> The contribution of organic compounds to cloud formation is still largely unclear but this chapter summarizes some of the current knowledge on the topic. The formation of liquid and ice clouds in the atmosphere takes place exclusively by condensation of water on aerosol particles called cloud condensation nuclei (CCN) or ice nuclei (IN),<sup>520</sup> respectively. In both cases, the large uncertainties in the climate budget are due to remaining gaps in the understanding of the microphysical processes controlling the condensation, in particular their selectivities towards specific atmospheric particles.<sup>519</sup> The formation of ice particles is even less understood than the one of liquid cloud droplets, but certain types of organic materials are known to be good IN, in particular biological material such as bacteria, spores, fungi, viruses, algae, and pollen.<sup>521</sup> However, the efficiency of this material as IN does not seem to be linked to its molecular properties but rather to its shape or geometry.

Nearly all the current knowledge on the formation of liquid cloud droplets from aerosol particles results from two types of instruments, built by the scientific community to study these processes: hygroscopicity tandem differential mobility analyzers (HTDMAs) and cloud condensation nuclei counters (CCNCs). These instruments sample the aerosol particles, exposing them to a controlled relative humidity over a certain residence time in a continuous flow chamber, and measuring either their growth due to water condensation in the chamber (with HTDMAs) or the number of activated

particles (with CCNCs).<sup>520</sup> The role of various aerosol components, in particular organic ones, on cloud droplet formation has been studied with these instruments in laboratory. Their measured efficiency is called “hygroscopicity”,<sup>520</sup> which is thus essentially an instrumental definition. While some organic compounds were found to be somewhat “hygroscopic”, such as organic acids and HULIS, to a few exceptions,<sup>522</sup> these instruments have not reported any effect of aerosol composition in the formation of cloud droplets in the atmosphere.<sup>523</sup>

There is however a significant gap between these instrumental observations and the theory describing the formation of cloud droplets from aerosol particles, the Köhler theory. In particular, the Köhler equation involves two parameters that can be affected by properties of organic compounds: the Raoult’s term, linking the concentration of solute and the water vapor pressure around the particle, and the surface tension of the particle. Consequently, the “hygroscopicity” measured by HTDMAs is a combination of both factors and thus not an intrinsic parameters of the processes. Furthermore, unlike the instrumental observations, the Köhler equation implies that cloud droplet formation should be favored by organic compounds increasing the Raoult’s term, thus dissociating in water, such as organic acids, and/or by those decreasing the surface tension of the particles, also called surfactants.

For this reason, the presence of organic surfactants in atmospheric particles was investigated already several decades ago.<sup>524</sup> But, because of the considerable analytical challenge they involved, these efforts resulted in a limited knowledge until recently. Some organic aerosol or fog fractions were however evidenced to affect the surface tension<sup>524-525</sup> but the compounds involved were not identified at the molecular level. Recently, the development of a more sophisticated extraction method targeting surface-active compounds allowed to isolate the total surfactant fraction of atmospheric aerosols and to characterize it.<sup>526</sup> This technique was used to evidence the

presence of much stronger surfactants than expected in ambient aerosols, and likely to have some impact on cloud formation. Dynamic investigations of aerosol surfactants also indicated their slow equilibration, exceeding the typical residence times of HTDMAs and CCNCs, and explaining the absence of surfactant effect observed with these instruments.<sup>526c</sup> The role of organic surfactants on cloud droplet formation is supported by a growing number of observations, such as the observation of surfactant effects on droplet formation for ambient aerosols measured with an HTDMA operating over longer timescales,<sup>522</sup> and in laboratory-generated aerosols.<sup>527</sup> The understanding of these processes and a definitive confirmation for the role of surfactants will require further studies, including the development of other instruments than HTDMAs and CCNCs, and various, complementary approaches. But only the molecular identification of aerosol surfactants, with advanced techniques such as LC/ESI-MS, will provide important information on the type of functions responsible for the surface-tension depletion, and the origin of these surfactants. In particular, the Critical Micelle Concentrations (CMC) estimated so far for aerosol surfactants suggest their microbial origin. This would need to be further investigated by comparing the molecular structures of these compounds with those of microbially-produced surfactant standards. Thus, even in this topic where microphysics and the physical chemical properties of compounds are important, molecular identification can provide unique, key information.

## **5.5. Nucleating compounds**

### **5.5.1. Introduction**

Nucleation is the process in which new solid or liquid particles form directly from gas phase species. It has been observed in nearly all regions and environments on Earth, from urban to remote locations, to the notable exception of mixed forests with high isoprene emissions such as the Amazonian rain forest<sup>528</sup> and clean Michigan forests.

In spite of these numerous atmospheric observations and a large number of laboratory investigations many unknowns remain in these processes. While sulfuric acid seems to be an essential component,<sup>529</sup> its atmospheric boundary layer concentration is generally too low to account for a simple binary nucleation with water vapor alone.<sup>530</sup> Other gases such as ammonia and organic compounds are thus suspected to be involved and enable nucleation under atmospheric conditions.<sup>531</sup>

To discuss the role of organic species in new particle formation in the atmosphere it is useful to differentiate between the very early steps of new particle formation (cluster or embryo formation, formation of a critical nucleus) and the growth of the critical nucleus to larger sizes ( $>2\text{-}3\text{ nm}$ ).<sup>532</sup> Today it is clear that organic species are heavily involved in the 2<sup>nd</sup> step (the growth process) but their importance in the formation of the critical nucleus is less clear. Although the contributions of physico-chemical and chemical processes cannot be clearly distinguished, the growth phase is generally described as being purely driven by the physico-chemical properties of the condensing compounds (i.e., their vapor pressure), while chemistry (chemical functionality) is more important for the formation of the cluster or embryo itself. But the role of organic compounds in particle nucleation and growth remains to be fully elucidated.

#### **5.5.2 Investigation of potential candidate molecules: Formation of the critical nucleus**

As mentioned above, chemical interactions are suspected to play an important role in the formation of the critical nucleus. These chemical interactions that draw the molecules from the gas to the condensed phase may span from ionic or covalent bond formation to mere electrostatic interactions.<sup>533</sup>

In the past few years the role of acid-base chemistry and salt formation in these processes has been the focus of investigations. In particular, organic amines emitted by soils and oceans have



been observed to enhance the nucleation of sulfuric acid by a base-stabilization mechanism involving acid-amine pairs.<sup>534</sup> A synergistic effect of amines and ammonia was also shown on the enhancement of sulfuric acid nucleation,<sup>535</sup> but the chemical mechanisms behind it remain unclear. Theoretical studies have indicated that similar strong interactions exist between dicarboxylic acids and amines in hydrated clusters, suggesting that they can participate in atmospheric aerosol nucleation by forming aminium carboxylate ion pairs.<sup>536</sup> This has been confirmed by the observation of aminium salts in nanometer atmospheric particles with thermal desorption-CI-MS.<sup>537</sup>

Laboratory studies<sup>514</sup> showed that glyoxal can contribute to the early particle growth of ultrafine sulfuric acid particles by non-oxidative processes such as oligomerization. In line with this, a nucleation process involving one molecule of sulfuric acid and one molecule of organic compound was suggested,<sup>531a</sup> which was recently supported by the observations of clusters of sulfuric acid and oxidation products of pinanediol in laboratory.<sup>538</sup> Laboratory measurements using atmospheric pressure inlet TOF-MS or CI-API-TOF-MS have also shown that highly oxidized organics play a central role in the early steps of cluster formation<sup>397,538-539</sup> but these techniques only provide the MW and empirical chemical formula of the observed compounds, but not their chemical functionality or structure.

### **5.5.3 Investigation of potential candidate molecules: Low-vapor pressure compounds**

One of the most important properties of organic compounds for new particle formation, both for the formation of the critical nucleus and for the growth of the particle, is their saturation vapor pressure. In a complex atmospheric particle the latter is influenced not only by the saturation vapor pressure of the pure compound, but also by the bulk composition of the particle and the particle curvature (Kelvin effect). Obviously the Kelvin effect is more important for the early steps of

particle formation (diameter < few nm). But the observed growth rates of small atmospheric particles could be matched by a box model by assuming that about half of the gas-phase oxidation products were non-volatile.<sup>540</sup> These calculations were refined<sup>541</sup> and showed that the equilibrium vapor pressures of the condensing organics must be as low as  $10^{-8}$  to  $10^{-7}$  Pa to account for the growth of sub-50-nm particles in continental forest environments.<sup>541-542</sup>

Since classical chemical oxidation mechanisms do not produce compounds with such low volatilities, their formation pathways are open to speculation. A first possible source for these extremely low volatile VOCs is the second-generation oxidation of semi-volatile VOCs by OH in the gas.<sup>543</sup> Molecular markers for second-generation products from biogenic VOC oxidation (e.g., MBTCA) have been observed in the field<sup>389b,544</sup> and in laboratory studies.<sup>543b,545</sup> But molecular information on 2<sup>nd</sup> or 3<sup>rd</sup> generation oxidation products of anthropogenic VOCs is lacking,<sup>546</sup> partly due to the lack of suitable markers retaining the original anthropogenic VOC skeleton.

Other potential low-vapor pressure candidates are higher-MW dimeric products from biogenic VOC oxidation. This was suggested by the observation of oxidation products of  $\alpha$ - and  $\beta$ -pinene displaying dimeric structures in laboratory-generated SOA and ambient fine particles using various HPLC/MS methods.<sup>40,372,377,547</sup> Their detailed molecular structures and hence their formation pathways is still subject to speculation. However, prominent high-MW dimers from  $\alpha$ -pinene ozonolysis (MW 368 and 358) have been structurally elucidated (Chapter 5.1). They were first thought to be non-covalent bonded dimers formed in the gas phase,<sup>370</sup> then later suggested to be products from condensed-phase reactions in SOA.<sup>389b</sup> An alternative explanation is that these high-MW dimers are formed by gas-phase reactions of stabilized Criegee Intermediates in the ozonolysis of terpenes, e.g.,  $\alpha$ -pinene.<sup>378</sup> This would make them plausible candidates for the early stage of nucleation in monoterpene-rich environments such as boreal forests.

Another potential contribution of organic molecules to particle formation and growth would be heterogeneous or multiphase reactions. Such reactions are known to lead to organic products with low volatility, such as organic acids (e.g., Kroll et al.<sup>367</sup>). Another example is heterogeneous formation of organosulfates,<sup>342a,344b,409a,548</sup> which are expected to have significantly lower vapor pressure than their precursors and would thus accelerate the growth of the ultrafine particles.

#### **5.5.4 Perspectives on nucleating organic compounds**

Despite a considerable number of studies and some advances in this topic over the last two decades, crucial gaps remain in the understanding of particle nucleation in the atmosphere, especially concerning the organic molecules involved in the formation of the critical nucleus and particle growth. Considerable work has focused on these processes in the boreal forest environment but there is a need for more investigations in other relevant environments such as tropical, marine, Arctic, and urban areas.

Progress in the understanding of these processes will depend directly on the possibility to improve current instrumentation and methods and achieve the unambiguous identification of the organic molecules involved. Key points of improvement should be the accuracy of the molecular identification, time resolution, and detection sensitivity. Another important point is these highly sensitive systems can be studied without changing gas-particle partitioning of semi-volatile compounds or chemical equilibria of heterogeneous processes.

#### **5.6. Organic intermediates**

The lifetime of organic compounds in the atmosphere spans over 6 orders of magnitudes, from seconds to decades, because of their wide range of reactivity with atmospheric oxidants and various removal processes. While most of this review addresses the identification of long-lived organic compounds, short-lived ones, acting as intermediates in reaction mechanisms, also play

important roles in atmospheric chemistry and are therefore important to identify and monitor. Both for the elucidation of the reaction mechanisms in laboratory and for the understanding and prediction of real atmospheric systems, some degree of molecular identification is necessary for these organic intermediates because their reactivity depends widely on their organic structure. But their detection and identification involves many more instrumental challenges than for stable ones. This chapter presents the most important examples of short-lived organic species in atmospheric chemistry, organic peroxy radicals and Criegee intermediates, and the solutions proposed so far for their monitoring and molecular identification. Some of the techniques presented are still largely under investigation and constitute by themselves emerging directions of research in this field.

#### **5.6.1. Organic peroxy radicals and the oxidizing capacity of the atmosphere**

##### **a) Importance of organic radicals in the oxidative capacity of the atmosphere**

Some of the main discoveries on the fundamental radical cycles in the atmosphere were made in 1970's: the OH radical was first identified as the main atmospheric oxidant,<sup>549</sup> and found to trigger the oxidation of organic gases and the production of organic peroxy radicals, "RO<sub>2</sub>", where R is an organic group.<sup>550</sup> The peroxy radicals HO<sub>2</sub> and RO<sub>2</sub>s were then found to play essential roles in the production of O<sub>3</sub> in the troposphere.<sup>3</sup> In the following decades these reactions were implemented in atmospheric models and, for a long time, the consistencies between modeled and observed O<sub>3</sub> concentrations gave the impression that these radical cycles were well understood. However, more recently, direct measurements of OH and HO<sub>2</sub> showed important discrepancies with models,<sup>551</sup> indicating that important parts of these cycles and, generally, of the oxidative (i.e., self-cleaning) capacity of the atmosphere were still not understood. Subsequent investigations suggested that the observed discrepancies were due to yet unknown reactions of the RO<sub>2</sub> radicals.<sup>507,551d,551e,552</sup> However, in spite of recent efforts to differentiate main classes of organic

peroxy radicals<sup>553</sup> (saturated and unsaturated ones), the lack of techniques able to distinguish different RO<sub>2</sub>s with specific organic structures (“speciated” measurements) strongly limit the investigation and definitive understanding of these chemical systems. But, because of their fundamental importance in the atmosphere, many techniques have been proposed to monitor RO<sub>2</sub>s,<sup>507,550a</sup> which are presented below.

#### **b) Observation techniques for RO<sub>2</sub> radicals**

The classical techniques to monitor RO<sub>2</sub>s, still widely employed in laboratory, are optical and magnetic spectroscopies, such as UV<sup>550a</sup> and IR<sup>554</sup> absorption spectroscopy, electron spin<sup>555</sup> and paramagnetic resonance (ESR and EPR). In particular, in spite of considerable technical challenges (sampling on ice at 77 K and off-line analyses) ESR was successfully applied to the detection of RO<sub>2</sub>s in the atmosphere.<sup>555</sup> However, a drawback of this technique, as well as with UV absorption, is that they only detect the radical center (-OO•) of RO<sub>2</sub>s, which is hardly affected by their organic structure, making the spectra unspecific.<sup>555a</sup> These techniques are thus mostly useful in laboratory, for the investigation of known radicals while, in the atmosphere, ESR provides total peroxy radical concentrations. IR absorption has been shown to be structure-specific<sup>554</sup> and used in laboratory for the characterization of various RO<sub>2</sub>s. However the applicability of this technique to complex systems such as the atmosphere remains to be demonstrated.

Other approaches were developed specifically for atmospheric detection, and remain today the main source of information on atmospheric RO<sub>2</sub>s. They are based on “chemical conversion”, which consists in converting all the RO<sub>2</sub>s into a single compound, easier to detect. A first version was the “peroxy radical chemical amplification” technique (PERCA), where the peroxy radicals were titrated with NO and the NO<sub>2</sub> produced was measured by luminescence.<sup>556</sup> Because of the interferences of other atmospheric compounds in the NO/NO<sub>2</sub> conversion alternative conversion

systems were proposed, such as ROxMAX and PerCIMS, where the radicals are titrated by  $^{34}\text{SO}_2$  to produce labeled  $\text{H}_2\text{SO}_4$ , in turn measured by MS.<sup>557</sup> Another variation is ROxLIF, where the  $\text{RO}_2\text{s}$  are converted into  $\text{HO}_2$ , then  $\text{OH}$ , which is measured by laser-induced fluorescence (LIF) or fluorescence assay by gas expansion (FAGE).<sup>558</sup> Recently, the FAGE approach was shown to be able to differentiate between saturated and unsaturated  $\text{RO}_2\text{s}$  (alkene- and aromatic-derived ones) based on their conversion kinetics.<sup>553</sup> While these techniques are valuable, as the only ones applicable to atmospheric  $\text{RO}_2\text{s}$  today, the conversion processes suppress most or all information on individual  $\text{RO}_2\text{s}$  and provide integrated signals (total  $\text{RO}_2$  concentrations). In addition, the response of the signals to individual  $\text{RO}_2\text{s}$  varies widely with their structure, as it depends on their reactivity in the conversion scheme. It is thus difficult to predict for unknowns atmospheric  $\text{RO}_2\text{s}$ . Finally, all these conversion schemes suffer from interferences in the atmosphere. These instrumental shortcomings are currently the main limitations to the full understanding of the atmospheric radical cycles.

Another group of techniques that show some promising potential for the speciated detection, thus the identification, of  $\text{RO}_2\text{s}$  in the atmosphere is mass spectrometry. As explained in the previous chapters, soft ionization techniques, avoiding fragmentation, provide MS signals directly reflecting the molecular weight of the analyte, with a potentially high level of identification for small masses ( $m/z < 300$ ) when using TOF mass filtration. The detection of short-lived species, however, precludes separation prior to sampling, which can limit this identification. Over the last decades a range of ionization schemes for  $\text{RO}_2\text{s}$  have been tested in laboratory: negative<sup>559</sup> and positive<sup>560</sup> photoionization, electron transfer with  $\text{SF}_6^-$ ,  $\text{O}_2^-$ , or an excited rare gas,<sup>561</sup> reaction with  $\text{I}^-$  or  $\text{O}_3^-$ ,<sup>562</sup> reaction with  $\text{O}_2^+$ ,<sup>563</sup> and proton transfer with  $\text{H}_3\text{O}^+$  and its water clusters. Many of these techniques, while useful in laboratory, are difficult to apply to atmospheric systems, either

because they require low-pressure samples or lead to the fragmentation of the RO<sub>2</sub>s. Only proton transfer with H<sub>3</sub>O<sup>+</sup> and its clusters appears to be suitable for atmospheric applications, as it avoids fragmentation and can be applied to atmospheric-pressure samples.<sup>564</sup> Until now, this approach for monitoring RO<sub>2</sub>s has only been used in laboratory, in most cases with set-ups where the reaction and ionization regions are integrated.<sup>564</sup> But adapting this technique to atmospheric sampling could be promising for the speciated detection of atmospheric RO<sub>2</sub>s and the investigation of the RO<sub>2</sub> and HO<sub>x</sub> radical cycles.

### 5.6.2. Criegee intermediates and ozonolysis

Ozonolysis is an important reaction for all unsaturated organic compounds in the atmosphere, both in the gas and at the surface of particles. Until very recently the lack of direct observation of its postulated intermediates, the Criegee intermediates, left many unknowns in atmospheric mechanisms because these intermediates are suspected to react with a number of atmospheric gases, such as H<sub>2</sub>O, SO<sub>2</sub>, NO, and NO<sub>2</sub>. In particular, their reaction with water vapor has been suggested as source for OH radicals, contributing directly to the atmospheric radical cycles. Recently, the use of synchrotron photoionization allowed to observe for the first time the simplest Criegee intermediates, CH<sub>2</sub>OO,<sup>565</sup> then CH<sub>3</sub>CHOO.<sup>566</sup> While these intermediates were not created in ozonolysis reactions, they allowed for the first direct measurements of their rate constants with important atmospheric species such as H<sub>2</sub>O, SO<sub>2</sub>, NO and NO<sub>2</sub>, and evidences some significant discrepancies with those estimated previously.<sup>565b,566-567</sup> In addition photoionization spectra allowed to distinguish the *anti* and *syn* isomers of CH<sub>3</sub>CHOO, and to evidence their very different reactivities with atmospheric gases.<sup>566</sup> More recently IR spectroscopy was also used for the detection of Criegee intermediates,<sup>568</sup> including in gas-phase ozonolysis reactions.<sup>569</sup> The

investigation of Criegee intermediates is now a rapidly expanding field of research, in which the development of techniques for their detection in the atmosphere will be an important direction.

### **5.6.3. Intermediate organic compounds in the atmospheric particulate phase**

As mentioned in previous chapters, the condensed-phase reactions of organic compounds in atmospheric aerosols have become an important field of investigation over the last two decades. The understanding of their mechanisms is important to determine the role of these reactions at regional and global scale. These mechanisms can be partly investigated by identifying specific markers, or by using some of the real-time techniques now available, such as aerosol MS (Section 4.1.2), monitoring the evolution of aerosol composition in the atmosphere.<sup>140,395</sup> However, these instruments record the chemical evolution by global parameters, such as O/C, H/C or ion ratios, and do not give access to mechanistic details. Similarly, the identification of stable reaction products, for instance by LC/MS techniques, is useful but not sufficient to elucidate the mechanisms, as many compounds can be obtained by different mechanisms. Examples of this are the current debates on whether the formation of organosulfates in atmospheric aerosols follows an ionic or radical mechanism, or the control of a range of organic reactions (condensation, acetalization, hydrolysis, etc.) by acid- or iminium ( $\text{NH}_4^+$ ) catalysis.<sup>409b,419a,420b,420c</sup> One approach to determine the contribution of different mechanisms to the chemical composition of aerosols can be to compare their respective product yields or isomeric ratios with those found in aerosols, as recently attempted.<sup>6,570</sup> However, this is only applicable if the products of interest are either stable or have identical reactivity in aerosols. But, as in gas-phase chemistry, the most direct and unambiguous way to probe the mechanisms would be to directly observe the organic intermediates. This would, however, involve a much higher level of difficulty than in the gas because of the small volumes of samples. Thus, to our knowledge, such direct observation has not been attempted yet



in atmospheric condensed phases, and might remain one of the ultimate challenges in atmospheric chemistry. However, because of their central importance for the understanding of the fate of organic carbon in aerosols, the mechanistic investigation of condensed-phase organic reactions is likely to be an important direction of research in the near future.

### **5.7. Health-hazardous compounds**

Besides the importance of atmospheric organic compounds for atmospheric chemistry and climate described in the previous Chapters, some of them also have toxic properties. The strongest evidence for the negative health effects of air pollution and, in particular of aerosol particles, result from epidemiological studies where short- or long-term exposure to increased levels of aerosol particles could be directly linked with pulmonary and cardio-vascular diseases, such as chronic obstructive pulmonary disease or asthma.<sup>571</sup> Numerous toxicological studies have linked adverse health outcomes to primary<sup>572</sup> as well as ambient aerosols.<sup>573</sup> Investigations of the chemical properties, molecular interactions and health effects of hazardous compounds in atmospheric aerosols have been recently summarized in reviews.<sup>574</sup>

Known toxic gases include inorganic compounds such as ozone, nitrogen oxides or carbon monoxide and a wide range of organic compounds such as small aromatics and aldehydes. Toxic particle-phase compounds represent an equally wide range, including transition metals and a large number of organics from polycyclic aromatic hydrocarbons to highly oxidizing compounds such as peroxides or radicals.<sup>575</sup>

While the toxicity of atmospheric particles has been established for decades the identity of the compounds contributing to the adverse health effects observed in epidemiological studies, and the role of aerosol composition in toxicity are still poorly understood. Some specific toxicity mechanisms have been identified for a limited number of compounds (PAHs) and revealed that

reactive metabolites such as diol epoxides of PAHs have the potential to bind to deoxynucleic acids and proteins causing genotoxicity and carcinogenicity. But such detailed mechanistic understanding is not available for most health-hazardous aerosol components. One obstacle to this understanding is the complexity of the particles directly emitted, combined with the complexity resulting from atmospheric processing,<sup>576</sup> making the identification of the compounds with adverse health effects a highly challenging task. Other reasons for this poor understanding are the low dose / long-term health effects of atmospheric particles rather than their acute toxicity and the wide range of susceptibility in the population, including potential pre-existing (e.g., respiratory) risk.

This chapter presents the analysis techniques used to identify and, more importantly for toxicity, quantify two main classes of toxic compounds in aerosol particles: PAHs, requiring structure-specific identification and trace-level quantification, and reactive oxygen species (ROS), representing a wide group of compounds. As discussed below these two classes of compounds correspond to very different *I*-factors.

PAHs were among the first compounds identified as toxic in air pollution particles, and are produced by fossil fuel combustion and biomass burning. They are present both in the gas and the condensed phase but the most toxic PAHs are particle-bound. Both parent-PAHs and oxidized and nitro-PAHs have been identified as toxic. A wide range of analytical techniques has been developed to separate and quantify individual PAHs in the gas and particle phase in the atmosphere. GCxGC methods<sup>271,268</sup> and LC techniques were specifically developed to investigate oxidized and nitro-PAHs,<sup>577</sup> but the reduced chromatographic resolution of LC methods compared to GC is often a limiting factor for the analysis of complex samples such as organic aerosols. MS is in many cases the detection technique of choice and a range of ionization methods were applied to PAHs. Electron ionization is most frequently used with GC but soft ionization methods such as

negative ion chemical ionization have also been applied to PAHs,<sup>578</sup> allowing for detection limits down to the low pg levels<sup>258</sup> and potentially also advanced structure identification via MS/MS. Recently, a thermal desorption GCxGC coupled with tandem mass spectrometry method reported detection limits in the sub-pg range for PAHs, oxidized and nitro-PAHs.<sup>467g</sup> LC offers a wider range of soft ionization methods than GC and APCI, in particular, achieves detection limits down to pg levels, thus lower than electrospray ionization.<sup>579</sup> Coupling chromatography and advanced MS techniques allows to identify PAHs with high certainty, even in highly complex atmospheric aerosol samples, often with *I*-factors close to unity.

MS techniques without chromatographic separation have also been applied to PAHs such as two-step laser mass spectrometry (L2MS). In this technique a first IR laser desorbs the organic material from the collection substrate (filter or impactor plate), and the second wavelength-specific UV laser selectively ionizes the PAHs.<sup>580</sup> By tuning the ionization laser to selectively ionize the PAHs, this technique avoids artifacts due to other organic compounds present in the sample. L2MS is however generally qualitative but a few attempts to use it in a quantitative way have been made and resulted in detection limits in the pg range.<sup>581</sup> Because L2MS is a one-dimensional technique its *I*-factor is inherently larger than for coupled techniques, and in the range of 10. Resonance-enhanced multiphoton ionization has also been successfully applied to detect PAH in thermally evolved gases from PM samples.<sup>582</sup>

Taking into account potential sampling artifacts is especially critical in the quantification of reactive compounds such as PAHs. Careful sampling procedures and controls are required to minimize their reaction on the sampling devices, which could lead to a severe underestimation of their concentrations.<sup>583</sup> Isotope dilution methods using <sup>13</sup>C- or <sup>2</sup>H-labelled PAHs as references are

frequently being used to improve precision and accuracy of the quantification of PAHs by reducing calibration, sample preparation and matrix problems.

However, because the toxicity of PAHs has been recognized for decades, long time series of PAHs atmospheric concentrations are available, especially at urban locations. In many regions the concentration of the most toxic ones, such as benzo[a]pyrene, has decreased by a factor of 10 over the last 30 years due to improved combustion technology. Yet respiratory diseases have steadily increased,<sup>584</sup> implying that other aerosol compounds or properties need to be considered for these chronic health effects. Reactive oxygen species have gained significant attention as potential health-hazardous compounds over the last years. ROS is a generic term for all oxidizing compounds in aerosols, including transition metals, inorganic oxidants such as OH and H<sub>2</sub>O<sub>2</sub>, and organic compounds such as quinones, organic peroxides and radicals.

The analysis of some organic ROS components is best achieved with the same analytical techniques as used for PAHs and presented above. Quinones, for example, have been quantified with GC/MS and LC/MS after derivatization, and resulted in detection limits in the pg range.<sup>585</sup> Other organic ROS such as (hydrogen-)peroxides and radicals are more difficult to analyze. Thus, analytical techniques have been developed to quantify the total concentration of ROS, or compound class such as peroxides, rather than individual compounds. The total concentration of all (hydrogen-)peroxides in organic aerosols was quantified using an iodometric method, and it was shown that a major fraction of the aerosol organic compounds generated in simulation chambers contains this functional group.<sup>575,586</sup> Other studies have successfully attempted to quantify the total concentration of organic radicals<sup>587</sup> by pro-fluorescent/fluorescent spin trap pairs, with detection limits in the low nmol/liter concentration range. On-line methods to quantify ROS have also been developed<sup>101</sup> and showed that some components have very short lifetimes, of only

a few minutes. This underlines the need to develop careful protocols to avoid artifacts due to particle collection and sample work up in the quantification of highly reactive compounds such as peroxides or radicals. Other recent efforts to characterize ROS in aerosols proposed a different approach by using surrogate biological systems, such as natural antioxidants ascorbic acid or glutathione, to quantify the effect of particle-bound ROS on the anti-oxidant capacity of human lung.<sup>588</sup> Thus, to the exception of the analysis of specific quinones, which can achieve an *I*-factor of 1, most of the recent techniques to characterize organic ROS focus on its quantification as a group of oxidizing compounds rather than as individual compounds. Thus the *I*-factor attributed to these techniques is large, of the order of  $I > 100$ .

In conclusion the analysis of health-hazardous organic compounds in the atmosphere is highly challenging. The difficulty lies not only in the identification and quantification of specific toxic compounds at trace levels but also in reproducing realistic exposure settings to simulate long time scales / low doses effects. For some compounds such as PAHs very advanced analytical methods have been established but other aspects of particle toxicity are still far from a compound-specific identification. The toxicity mechanisms of many other organic aerosol components are even less characterized and toxic and oxidative stress (triggered by ROS uptake or by the generation of ROS in the body) mechanisms are expected to be multiple.<sup>589</sup> Future research in this area will thus need to establish quantitative relationships between a wide range of potentially toxic components in atmospheric aerosols and health effects, and to make more efforts to identify the toxicity resulting from specific compounds. Only such a compound-specific knowledge will ultimately allow to identify the relevant sources and to develop emission reduction strategies.

## **6. Conclusion and perspectives**

From an analytical point of view, exploring the chemical composition of the atmosphere and the chemical processes taking place in it involves as many unknowns, and nearly as many challenges, as exploring other unknown environments, such as the deep oceans or other planets. The numerous techniques presented in this review illustrate the tremendous increase of interest over the last decades for atmospheric constituents that are characteristic for our planet, organic compounds, and the considerable progress accomplished in the analytical tools allowing to study them. To overcome the numerous challenges presented by atmospheric problems, this progress has required not only the use of existing techniques from other disciplines, but also their adaptation to atmospheric applications and the development of entirely new techniques. In about three decades these techniques have brought a much clearer picture, both qualitatively and quantitatively, of the myriad of organic compounds present in the atmosphere, their sources, and their contribution to important processes such as air quality, the ozone cycle, and SOA formation. Over an even shorter period of time (the last two decades) the tools developed to study organic compounds in the atmospheric condensed-phases (e.g., aerosols and clouds) have revealed the wide complexity of these media and allowed to characterize their sources and compositional changes over their atmospheric lifetime by the identification of markers, in particular for biogenic and biomass burning SOA. Understanding the tight connection between gas- and particle-phase chemistries, the resulting SOA formation, and their contributions to atmospheric chemistry and climate have thus undergone significant advances and better descriptions can be anticipated in the near future.

However, two main factors hamper this progress. One of them is the analytical expertise needed to identify organic compounds. In particular, non-specialists tend to overestimate the level of identification of organic compounds provided by a specific analytical technique, leading to reports of unverified or false compounds or processes. We hope that the discussion of the identification

capabilities of the different techniques presented in this review will avoid such shortcomings and stimulate interdisciplinary collaborations between atmospheric scientists of very different backgrounds to explore complex chemical atmospheric processes in the future.

Another main difficulty is the analytical challenge presented by some compounds that are central in some key atmospheric processes. Examples of processes being barely in reach of current analytical capabilities today are given in Chapter 5: the role of organic compounds in nucleation, cloud formation, the aging of aerosol components, the formation of health-hazardous particles, and, via peroxy and Criegee intermediates, the oxidizing cycles of the atmosphere. The investigation of these processes will require further analytical developments, some of which are underway, and which could also benefit other chemical disciplines.

## FIGURE CAPTIONS

**Figure 1.** The application of the retrosynthetic analysis for the design of the synthetic pathways leading to 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), a relevant marker for  $\alpha$ -pinene SOA aging.<sup>36</sup>

**Figure 2.** Estimated atmospheric lifetimes of selected SOA marker compounds according to their volatility.<sup>590</sup>

**Figure 3:** Summary of the most abundant analytical chemical techniques used to characterize organic compounds in the atmosphere as function of *I* factor. A decreasing *I* factor describes the increasing capability of a technique to identify the molecular structure of a compound. The y-axis describes the ability of a technique to characterize the entire organic mass present in the atmosphere. Coupling of two techniques (mainly involving chromatography) allows for a significantly increased *I* factor. Techniques frequently coupled to chromatography or suitable to coupling with chromatography are shown in blue, others in red.

**Figure 4.** Illustration of the effect of various atmospheric processes on the  $\delta^{13}\text{C}$  of carbonaceous aerosols. Blue arrows denote depletion in the heavy isotope (lowering of the  $\delta^{13}\text{C}$ ), red arrows denote enrichment (increasing  $\delta^{13}\text{C}$ ) and green arrows indicate processes that may change in both directions. Reprinted with permission from ref. 179. Copyright 2013 American Geophysical Union and John Wiley & Sons, Inc.



**Figure 5.** Contour plot of the total ion current chromatogram of an urban aerosol sample examined by GCxGC–TOFMS (left) and the mass spectrum of a compound to identify aerosol constituents (right). Reprinted with permission from ref. 272. Copyright 2013 Elsevier.

**Figure 6.** Examples of organic acids formed in the oxidation of methylglyoxal and analyzed using IC/ESI-MS. a. IC-ESI mass spectra of a mixed standard of acids: (A) acetic (not detected in ESI-MS) and glycolic ( $m/z$  75), (B) formic (not detected in ESI-MS), (C) pyruvic ( $m/z$  87), (D) glyoxylic ( $m/z$  73), (E) succinic ( $m/z$  117), (F) malonic ( $m/z$  103), (I) oxalic ( $m/z$  89). b-d. IC-ESI-MS spectra of acids at increasing concentrations of methylglyoxal. b. 30  $\mu$ M: (A) the retention time ( $t_r$ ) of acetic/glycolic acids, (B)  $t_r$  of formic acid, (C) pyruvic acid, (I) oxalic acid, (J) mesoxalic acid ( $m/z^-$  117). c. 300  $\mu$ M: (A + B)  $t_r$  of acetic/glycolic acids + formic acid, (C) pyruvic acid, (I) oxalic acid, (J) mesoxalic acid. d. 3000  $\mu$ M: (A + B + C)  $t_r$  of acetic/glycolic acids + formic acid + pyruvic acid, (E)  $t_r$  of succinic acid, (F)  $t_r$  of malonic acid, (I) oxalic acid. Reprinted with permission from ref. 305a. Copyright 2010 Elsevier.

**Figure 7:** van Krevelen plots for molecular formulas assigned to FTICR mass spectra peaks in aerosol samples from a) New York and b) Virginia. Blue diamonds represent compounds containing only C, H, and O, yellow squares represent S-containing compounds, and red triangles are N-containing compounds. Black ovals represent traditional potential source molecular classes. The green SOA oval represents data from laboratory investigations of SOA. Adapted from Ref.<sup>351</sup>

**Figure 8:** (–)ESI-ion trap MS data for a prominent high-MW 358 dimer present in  $\alpha$ -pinene ozonolysis SOA, assigned to a pinyl diaterpenyl ester: (A) first-order mass spectrum; (B)  $m/z$  357

MS<sup>2</sup> spectrum; (C1) and (C2)  $m/z$  357  $\rightarrow$   $m/z$  171 MS<sup>n</sup> (n = 3, 4) spectra; and (D1) and (D2)  $m/z$  357  $\rightarrow$   $m/z$  185 MS<sup>n</sup> (n = 3, 4) spectra. The MS<sup>n</sup> data obtained by fragmentation of  $m/z$  171 establish that diaterpenylic acid is a monomeric unit, whereas those obtained by fragmentation of  $m/z$  185 identify *cis*-pinic acid as a second monomeric unit, since exactly the same MS patterns are found by fragmenting deprotonated terpenylic and *cis*-pinic acids. Adapted from: Yasmeen et al.<sup>40</sup>

**Figure 9.** Contributions of different sources, in particular of the photolysis of organic gases (circled in red) to the radical budget in Mexico City during the MCMA-2006 campaign.<sup>509</sup>  
Acronyms: MGLY, methylglyoxal; GLY, glyoxal; ALD, aldehydes.

**Figure 1**

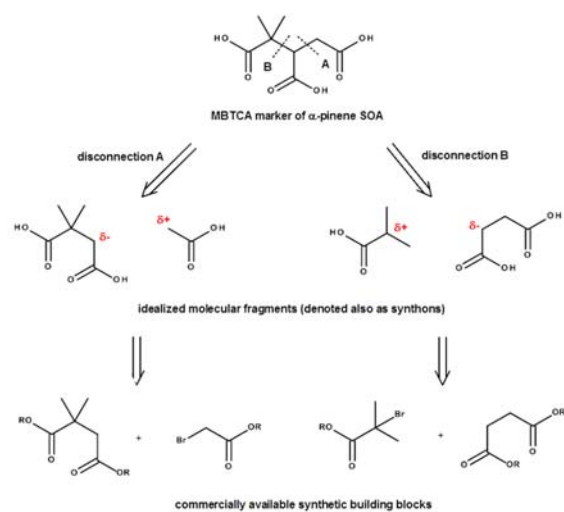
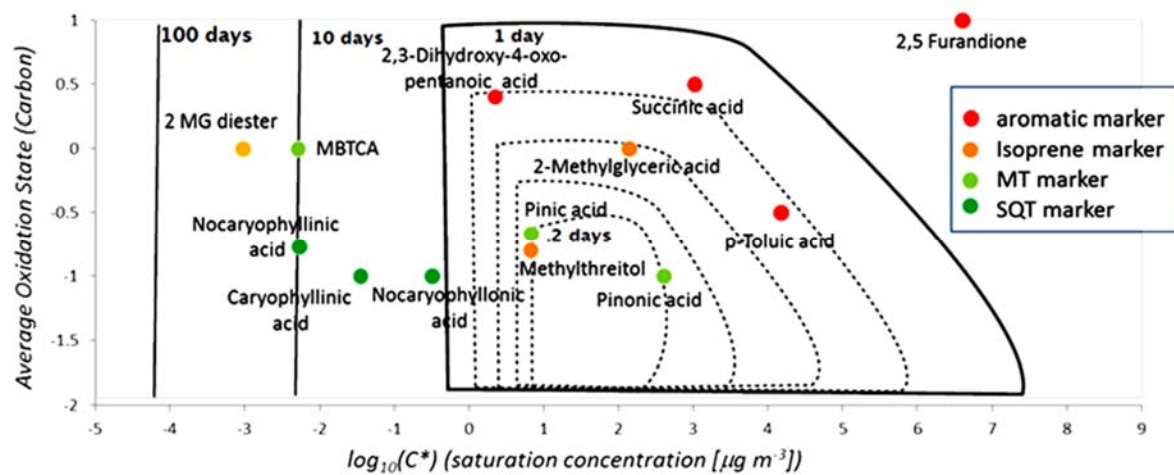


Figure 2



**Figure 3**

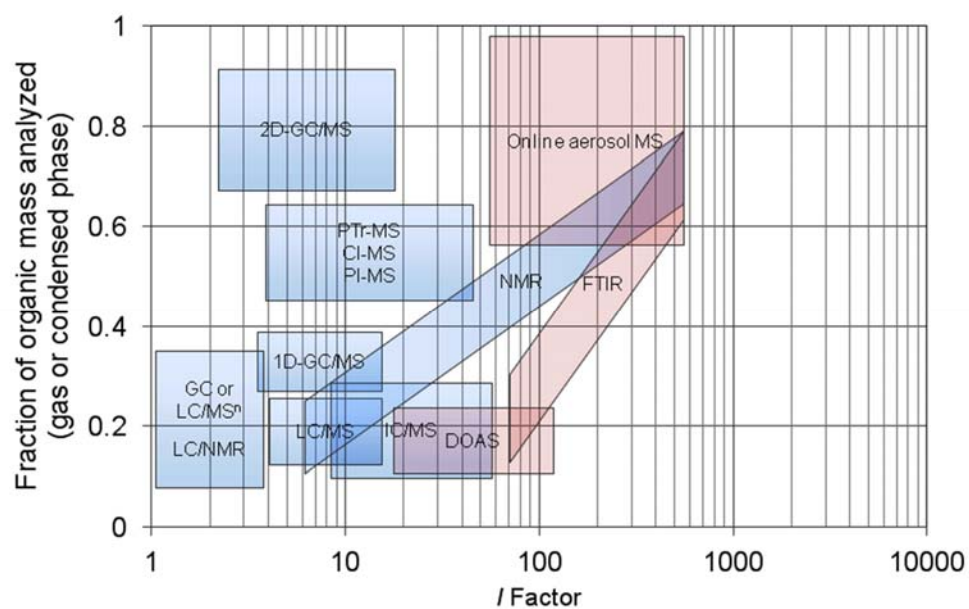
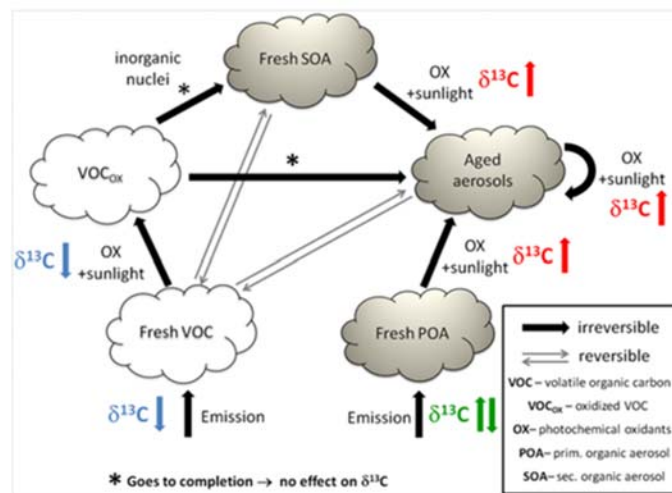


Figure 4



**Figure 5**

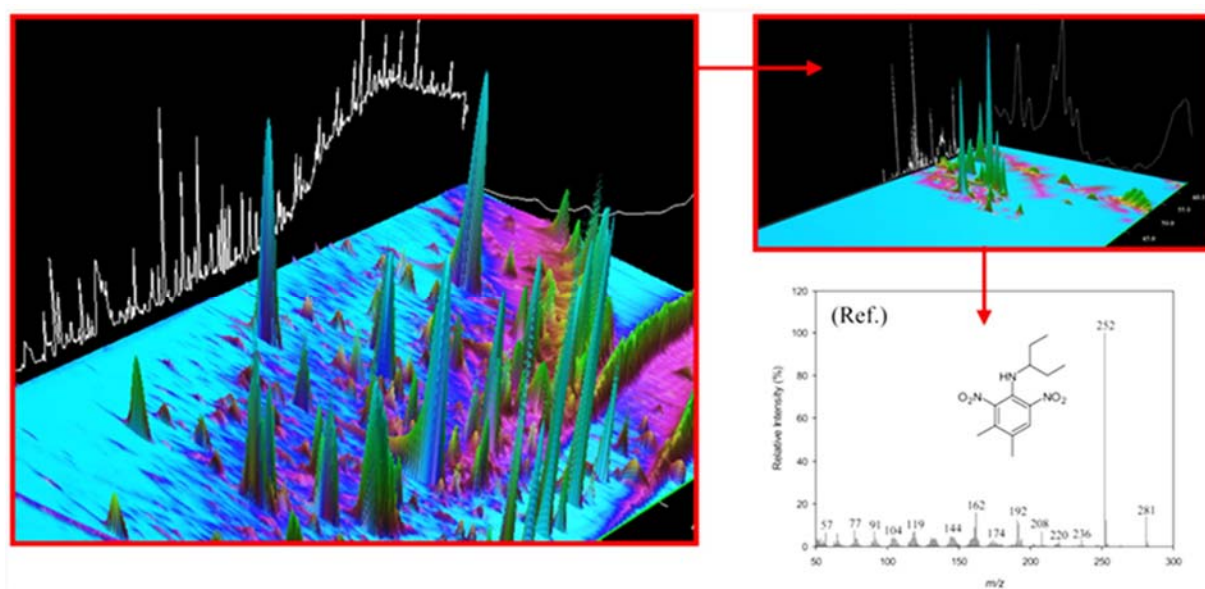


Figure 6

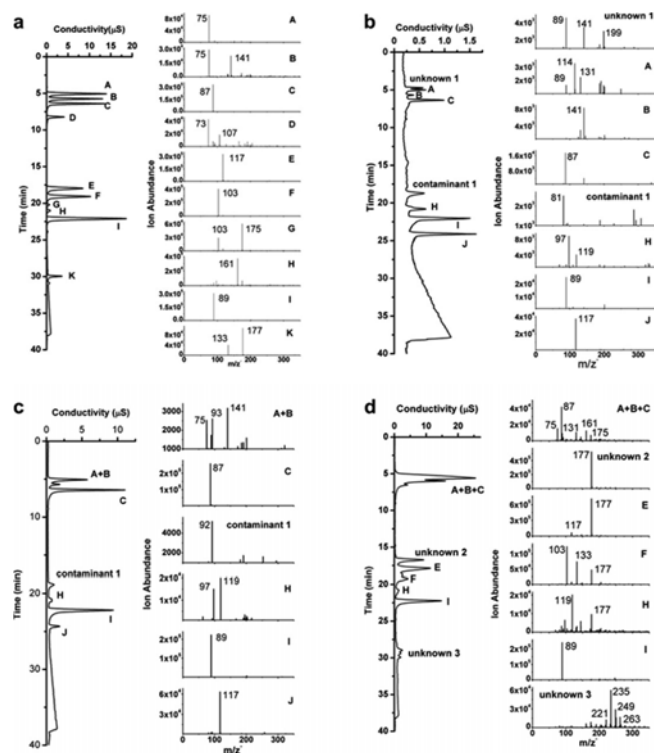
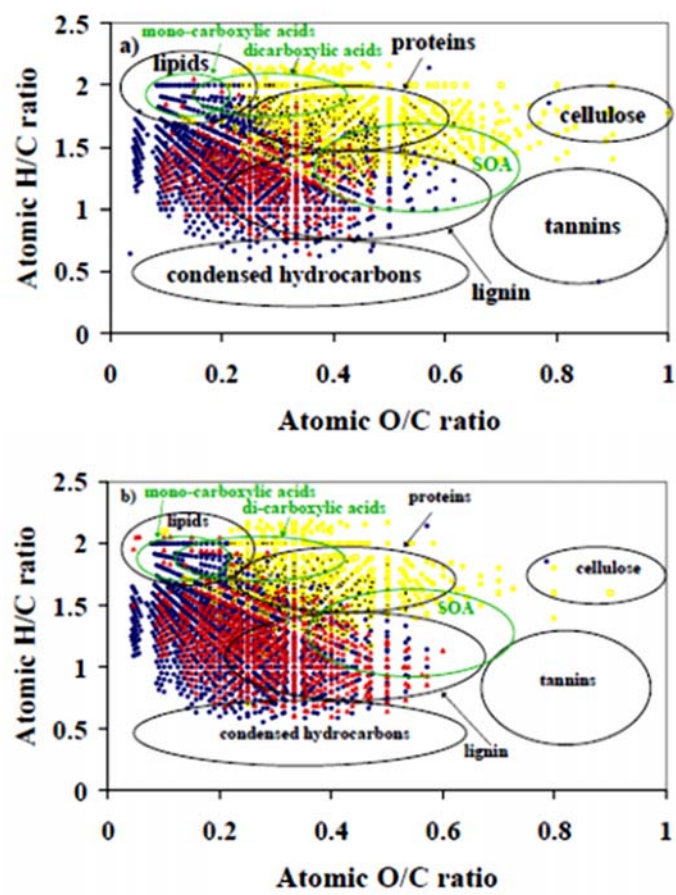




Figure 7



**Figure 8**

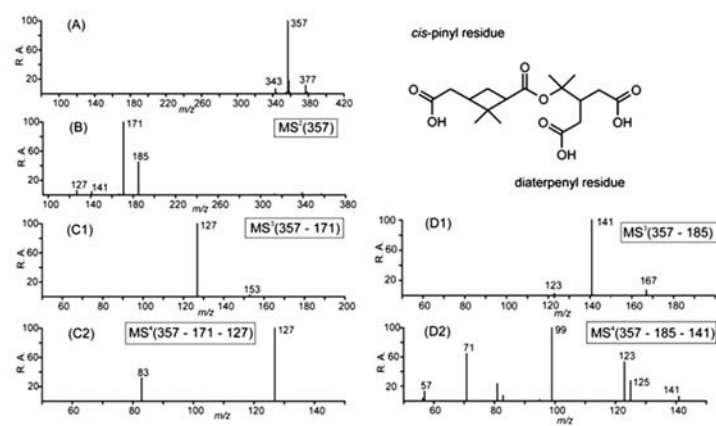
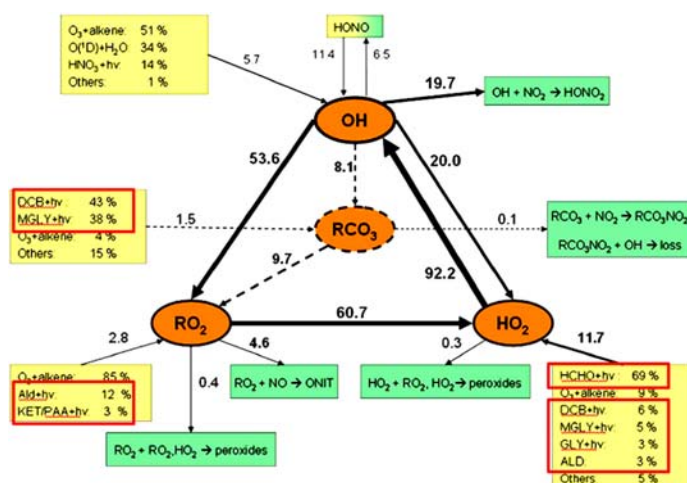


Figure 9



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Markus Kalberer studied Environmental Sciences at the Eidgenössische Technische Hochschule (ETH), Zurich, and obtained a Ph.D. in Chemistry from the University of Bern (both in Switzerland) in 1998. He subsequently performed postdoctoral studies at the California Institute of Technology in Pasadena, USA. He returned to Switzerland for a Habilitation at ETH, Zurich, and is now Reader in Atmospheric Sciences at the University of Cambridge, UK. His research interests include the formation, reactivity, and composition of organic aerosols, and the investigation of negative health effects of atmospheric particles with chemical and cell culture studies.



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Magda Claeys received a Ph.D. in Chemistry from Ghent University, Belgium, in 1974, with research on bio-organic mass spectrometry. Since 1978 she is affiliated with the University of Antwerp, where she held research positions supported by the Research Foundation Flanders (FWO), was promoted to full professor in 2000, and since 2013 continues her research as an emeritus professor. She has a long-standing experience with organic analytical mass spectrometry and centered on biomolecular mass spectrometry during her early career. For the last 20 years her research focused on the molecular characterization and speciation of atmospheric aerosols. A

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Emanuela Finessi obtained a Ph.D. in Chemistry from the University of Bologna, Italy, in 2010, on the chemical characterization of organic aerosol and source identification. She has over seven years of research experience in atmospheric chemistry, working on a broad range of collaborative projects within both field and simulation chamber experiments. Her research interests include processes related to the formation, transformation and fate of organic aerosol, brown carbon and organic nitrogen species in atmospheric particles. Since joining the University of York, UK, in 2011, she has focused on the aqueous processing of reactive carbonyls and interactions with inorganics by using a wide range of mass spectrometric techniques. Recent activities include the development of sensitive and selective methods for the determination of trace organic nitrogen species in complex matrices.



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Jacqueline Hamilton obtained a Ph.D. in Chemistry from the University of Leeds in 2003. She was appointed a Lecturer in Atmospheric Chemistry at the University of York in 2008. She has developed independent research themes in atmospheric aerosol chemistry underpinning a variety of laboratory, simulation chamber and field observations. She has a strong interest in analytical science, developing methods and instrumentation in comprehensive two-dimensional gas chromatography (GCXGC), HPLC/MS and high-resolution Fourier transform ion cyclotron

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Thorsten Hoffmann obtained a Ph.D. in Chemistry from the University of Dortmund, Germany, in 1992. Since 2003 he is Professor of Analytical Chemistry at the Johannes Gutenberg-University of Mainz, Germany. His main research activities are the design and development of tailored methods to chemically characterize biological and environmental matrices. The motivation is a better understanding of biosphere-atmosphere interactions, e.g., by the investigation of the sources, formation pathways and chemical transformation of biogenic aerosol particles, or the development of trace analytical techniques to investigate climate archives (ice cores, speleothems). Most of the analytical research is focused on organic analytes in combination with mass spectrometry (GC/MS, LC/MS) with a certain emphasis on the development of real-time methods for atmospheric aerosol characterization (aerosol mass spectrometry).



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Yoshiteru Iinuma received a Ph.D. in Physics with focus on physical and chemical characterization of atmospheric aerosols from the University of New South Wales, Sydney, Australia, in 2002. He joined the Leibniz Institute for Tropospheric Research (TROPOS) in Leipzig, Germany, as a postdoctoral fellow, and in 2008 he became a research scientist at TROPOS. His main research focuses on the physical and chemical characterization of both the gaseous and particulate organic compounds in field and laboratory-generated samples using various chromatographic and mass spectrometric techniques.



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Ariane Kahnt studied Pharmacy at the University of Halle, Germany, and obtained a Ph.D. in Natural Sciences from the University of Leipzig, Germany, in 2012. During her Ph.D. research she studied atmospheric oxidation products and SOA formation from monoterpene ozonolysis under the supervision of Professor Hartmut Herrmann. After postdoctoral studies at the University of Antwerp, Belgium, where she continued to identify organic compounds in atmospheric aerosol samples using mass spectrometric techniques, she recently joined the Faculty of Biology at the University of Auckland, New Zealand. Her current research involves genomic, proteomic and metabolomic analysis using mass spectrometry.



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Christopher J. Kampf studied Chemistry at the Johannes Gutenberg-University Mainz, Germany, where he also did his Ph.D. work in the group of Professor Thorsten Hoffmann and obtained a Ph.D. degree in 2012. His Ph.D. work dealt with the characterization and quantification of reactive dicarbonyl compounds in atmospheric aerosols. Afterwards he carried out postdoctoral research at the University of Colorado, Boulder, USA, before starting as a project leader for Analytical Chemistry of Proteins and Organic Aerosols at the Max Planck Institute for Chemistry in Mainz. His current research focuses on the identification of proteins in atmospheric aerosols by means of state-of-the-art mass spectrometry, elucidation of protein modifications and degradation processes introduced by air pollutants, as well as formation processes of light absorbing compounds in secondary organic aerosols.



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Ivan Kourtchev studied Chemistry at the Mendeleyev University of Chemical Technology of Russia, Moscow, graduating with an Engineering degree (B.Sc. equivalent) in 1997. After spending two years at the home institution as an engineer, he continued his studies at Oklahoma State University, USA, graduating in 2002 with a M.Sc. in Biosystems Engineering. He subsequently performed Ph.D. studies at the University of Antwerp, Belgium, on the molecular characterization of atmospheric aerosols and obtained a Ph.D. in Chemistry in 2008. His research interests in analytical and physical chemistry strengthened after postdoctoral stays at University College Cork, Ireland, and the Joint Research Centre of European Commission, Belgium. In 2011 he was awarded a Marie Curie Fellowship to perform research in high resolution mass spectrometry and atmospheric chemistry at the University of Cambridge, UK, where he is currently employed as a research associate.



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Willy Maenhaut is an atmospheric and analytical chemist. In 1972 he obtained a Ph.D. degree in Chemistry from Ghent University, Belgium. He has over 45 years of experience in atmospheric chemistry, with emphasis on (experimental) atmospheric aerosol research. He is (co-)author of



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organosulfate formation from the atmospheric oxidations of isoprene and monoterpenes, and thus, providing a set of molecular markers for secondary organic aerosols of a mixed biogenic/anthropogenic origin.



Sönke Szidat

Sönke Szidat received a Ph.D in Chemistry from the University of Hannover, Germany, in 2000, having carried out research on the long-lived radioisotope  $^{129}\text{I}$  in the environment. He performed postdoctoral research at the University of Bern, Switzerland. In 2007, he became group head and lecturer at the University of Bern. He received the Atmospheric Chemistry and Physics (ACP) Award of the ACP Commission of the Swiss Academy of Sciences in 2008, the Fritz-Strassmann-Preis of the Nuclear Chemistry Division of the German Chemical Society in 2009, and the habilitation at the University of Bern in 2009. He is the head of the Laboratory for the Analysis of Radiocarbon with accelerator mass spectrometry at Bern since 2013. His research interests are measurements of the long-lived radioisotope  $^{14}\text{C}$  in the environment with focus on source apportionment of carbonaceous aerosols.



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Rafal Szmigielski received a M.Sc. in Chemistry from Warsaw University of Technology, Poland, in 1999, whereupon he joined the Institute of Organic Chemistry of the Polish Academy of Sciences (PAS) and obtained a Ph.D. in 2004 with research on gas-phase ion chemistry. He performed postdoctoral research at the same institute and between 2006 and 2009 at the University of Antwerp, Belgium. There, he became involved in the molecular characterization of SOA using mass spectrometry and was awarded a Marie Curie Fellowship. A highlight of his career was the discovery of 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), a marker for aged  $\alpha$ -pinene SOA. Since 2010 he is affiliated with the Institute of Physical Chemistry of the PAS, where he heads the Laboratory of Environmental Chemistry and continues studying SOA formation and processing using hyphenated techniques and organic synthesis.



Armin Wisthaler received a Ph.D. in Physics in 2001 from the University of Innsbruck, where he subsequently worked as a postdoctoral fellow and assistant professor. He was employed as a Senior Scientist at the Norwegian Institute of Air Research (NILU) between 2011 and 2013 before being appointed Professor of Atmospheric Chemistry at the University of Oslo in 2014. His expertise includes ion chemistry and chemical ionization mass spectrometry (in particular PTR-MS) as well as atmospheric chemistry.

## ABBREVIATIONS

ACS	American Chemical Society
AMS	aerosol mass spectrometer
API	atmospheric pressure ionization
APCI	atmospheric pressure chemical ionization
ASMS	American Society for Mass Spectrometry
ATOFMS	aerosol time-of-flight mass spectrometer
BBOA	biomass burning organic aerosol
BVOC	biogenic volatile organic compound
C <sub>n</sub>	organic compound with n carbon atoms
CCN	cloud condensation nuclei
CCNC	cloud condensation nuclei counter
CE	capillary electrophoresis
CFC	chlorofluorocarbon
CI	chemical ionization
CMB	chemical mass balance
CRDS	cavity ring down spectroscopy
2D	two-dimensional

Da	Dalton
DBE	double bond equivalent
DCA	dicarboxylic acid
DESI	desorption electrospray ionization
DOAS	differential optical absorption spectroscopy
EC	elemental carbon
ECD	electron capture detector
EI	electron ionization
ESI	electrospray ionization
FAGE	fluorescence assay by gas expansion
FID	flame ionization detector
FTICR	Fourier transform ion cyclotron
FTIR	Fourier transform infrared spectroscopy
GC	gas chromatography
GCxGC	two-dimensional GC
GHG	greenhouse gas
HCFC	hydrochlorofluorocarbon



HFC	hydrofluorocarbon
HILIC	hydrophilic interaction liquid chromatography
HOA	hydrocarbon-like organic material
HO <sub>x</sub>	OH + HO <sub>2</sub>
HPAEC	high-performance anion-exchange chromatography
HPLC	high-performance liquid chromatography
HR	high-resolution
HTDMA	hygroscopicity tandem differential mobility analyzer
HULIS	humic-like substances
IC	ion chromatography
ILC	interlaboratory comparison
IPCC	Intergovernmental Panel for Climate Change
IR	infrared
IUPAC	International Union for Pure and Applied Chemistry
KIE	kinetic isotope effect
KM	Kendrick mass
L2MS	two-step laser mass spectrometry

LC	liquid chromatography
LDI	laser desorption/ionization
LP	long-path
LV	low-volatility
MBTCA	3-methyl-1,2,3-butanetricarboxylic acid
MCA	multi-component analysis
MS	mass spectrometry
MS/MS or MS <sup>n</sup>	tandem mass spectrometry
MW	molecular weight
<i>m/z</i>	mass-to-charge ratio
NMR	nuclear magnetic resonance
NO <sub>x</sub>	nitrogen oxides (NO + NO <sub>2</sub> )
OC	organic carbon
OOA	oxygenated organic material
OSc	carbon oxidation state
PAH	polyaromatic hydrocarbon
PBAP	primary biogenic aerosol particle

PAD	pulsed amperometric detection
PAN	peroxyacyl nitrate
PI	photoionization
PILS	particle-into-liquid sampler
PM <sub>n</sub>	particulate matter with an aerodynamic diameter $\leq n$ $\mu\text{m}$
PMF	positive matrix factorization
POA	primary organic aerosol
Q	quadrupole
ppm	parts per million
ppb	parts per billion
ppt	parts per trillion
RO <sub>2</sub>	peroxy radical
ROS	reactive oxygen species
SOA	secondary organic aerosol
SV	semi-volatile
TAG	thermal desorption aerosol gas chromatography
TC	total carbon

TOF	time-of-flight
UHR	ultra-high resolution
UPLC	ultra-performance LC
UV	ultra-violet
Vis	visible
VK	van Krevelen
VOC	volatile organic compound
VUV	vacuum ultra-violet
WSOC	water-soluble organic carbon

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